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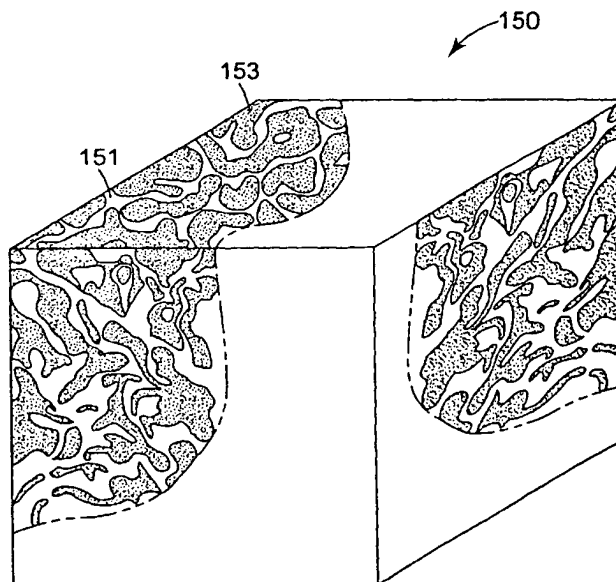
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(54) Title: FUSED  $Al_2O_3$ - $Y_2O_3$  EUTECTIC ABRASIVE PARTICLES, ABRASIVE ARTICLES, AND METHODS OF MAKING AND USING THE SAME



(57) Abstract: Fused abrasive particles comprising alumina (151)-aluminium yttrium oxide (153) composite eutectic material (150). The fused abrasive particles can be incorporated into abrasive products such as coated abrasives, bonded abrasives, non-woven abrasives, and abrasive brushes.

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## FUSED $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$ EUTECTIC ABRASIVE PARTICLES, ABRASIVE ARTICLES, AND METHODS OF MAKING AND USING THE SAME

5

### Field of the Invention

This invention pertains to fused abrasive particles and methods of making the same. The fused abrasive particles can be incorporated into a variety of abrasive articles, including bonded abrasives, coated abrasives, nonwoven abrasives,  
10 and abrasive brushes.

### Description of Related Art

There are a variety of abrasive particles (e.g., diamond particles, cubic boron nitride particles, fused abrasive particles, and sintered, ceramic abrasive particles  
15 (including sol-gel-derived abrasive particles) known in the art. In some abrading applications, the abrasive particles are used in loose form, while in others the particles are incorporated into abrasive products (e.g., coated abrasive products, bonded abrasive products, non-woven abrasive products, and abrasive brushes). Criteria used in selecting abrasive particles used for a particular abrading application include: abrading  
20 life, rate of cut, substrate surface finish, grinding efficiency, and product cost.

From about 1900 to about the mid-1980's, the premier abrasive particles for abrading applications such as those utilizing coated and bonded abrasive products were typically fused abrasive particles. There are two general types of fused abrasive particles: (1) fused alpha alumina abrasive particles (see, e.g., U.S. Pat. Nos. 1,161,620  
25 (Coulter), 1,192,709 (Tone), 1,247,337 (Saunders et al.), 1,268,533 (Allen), and 2,424,645 (Baumann et al.)) and (2) fused (sometimes also referred to as "co-fused") alumina-zirconia abrasive particles (see, e.g., U.S. Pat. Nos. 3,891,408 (Rowse et al.), 3,781,172 (Pett et al.), 3,893,826 (Quinan et al.), 4,126,429 (Watson), 4,457,767 (Poon et al.), and 5,143,522 (Gibson et al.))(also see, e.g., U.S. Pat. Nos. 5,023,212 (Dubots  
30 et. al) and 5,336,280 (Dubots et.al) which report the certain fused oxynitride abrasive particles). Fused alumina abrasive particles are typically made by charging a furnace with an alumina source such as aluminum ore or bauxite, as well as other desired

additives, heating the material above its melting point, cooling the melt to provide a solidified mass, crushing the solidified mass into particles, and then screening and grading the particles to provide the desired abrasive particle size distribution. Fused alumina-zirconia abrasive particles are typically made in a similar manner, except the furnace is charged with both an alumina source and a zirconia source, and the melt is more rapidly cooled than the melt used to make fused alumina abrasive particles. For fused alumina-zirconia abrasive particles, the amount of alumina source is typically about 50-80 percent by weight, and the amount of zirconia, 50-20 percent by weight zirconia. The processes for making the fused alumina and fused alumina abrasive particles may include removal of impurities from the melt prior to the cooling step.

Although fused alpha alumina abrasive particles and fused alumina-zirconia abrasive particles are still widely used in abrading applications (including those utilizing coated and bonded abrasive products, the premier abrasive particles for many abrading applications since about the mid-1980's are sol-gel-derived alpha alumina particles (see, e.g., U.S. Pat. Nos. 4,314,827 (Leitheiser et al.), 4,518,397 (Leitheiser et al.), 4,623,364 (Cottringer et al.), 4,744,802 (Schwabel), 4,770,671 (Monroe et al.), 4,881,951 (Wood et al.), 4,960,441 (Pellow et al.), 5,139,978 (Wood), 5,201,916 (Berg et al.), 5,366,523 (Rowenhorst et al.), 5,429,647 (Larmie), 5,547,479 (Conwell et al.), 5,498,269 (Larmie), 5,551,963 (Larmie), and 5,725,162 (Garg et al.)).

The sol-gel-derived alpha alumina abrasive particles may have a microstructure made up of very fine alpha alumina crystallites, with or without the presence of secondary phases added. The grinding performance of the sol-gel derived abrasive particles on metal, as measured, for example, by life of abrasive products made with the abrasive particles was dramatically longer than such products made from conventional fused alumina abrasive particles.

Typically, the processes for making sol-gel-derived abrasive particles are more complicated and expensive than the processes for making conventional fused abrasive particles. In general, sol-gel-derived abrasive particles are typically made by preparing a dispersion or sol comprising water, alumina monohydrate (boehmite), and optionally peptizing agent (e.g., an acid such as nitric acid), gelling the dispersion, drying the gelled dispersion, crushing the dried dispersion into particles, screening the

particles to provide the desired sized particles, calcining the particles to remove volatiles, sintering the calcined particles at a temperature below the melting point of alumina, and screening and grading the particles to provide the desired abrasive particle size distribution. Frequently a metal oxide modifier(s) is incorporated into the sintered  
5 abrasive particles to alter or otherwise modify the physical properties and/or microstructure of the sintered abrasive particles.

There are a variety of abrasive products (also referred to "abrasive articles") known in the art. Typically, abrasive products include binder and abrasive particles secured within the abrasive product by the binder. Examples of abrasive  
10 products include: coated abrasive products, bonded abrasive products, nonwoven abrasive products, and abrasive brushes.

Examples of bonded abrasive products include: grinding wheels, cutoff wheels, and honing stones). The main types of bonding systems used to make bonded abrasive products are: resinoid, vitrified, and metal. Resinoid bonded abrasives utilize  
15 an organic binder system (e.g., phenolic binder systems) to bond the abrasive particles together to form the shaped mass (see, e.g., U.S. Pat. Nos. 4,741,743 (Narayanan et al.), 4,800,685 (Haynes et al.), 5,038,453 (Narayanan et al.), and 5,110,332 (Narayanan et al.)). Another major type are vitrified wheels in which a glass binder system is used to bond the abrasive particles together mass (see, e.g., U.S. Pat. Nos. 4,543,107 (Rue),  
20 4,898,587 (Hay et al.), 4,997,461 (Markhoff Matheny et al.), and 5,863,308 (Qi et al.)). These glass bonds are usually matured at temperatures between 900°C to 1300°C. Today vitrified wheels utilize both fused alumina and sol-gel-derived abrasive particles. However, fused alumina-zirconia is generally not incorporated into vitrified wheels due in part to the thermal stability of alumina-zirconia. At the elevated temperatures at  
25 which the glass bonds are matured, the physical properties of alumina-zirconia degrade, leading to a significant decrease in their abrading performance. Metal bonded abrasive products typically utilize sintered or plated metal to bond the abrasive particles.

The abrasive industry continues to desire abrasive particles and abrasive products that are easier to make, cheaper to make, and/or provide performance  
30 advantage(s) over conventional abrasive particles and products.

Summary Of The Invention

The present invention provides a fused, crystalline abrasive particle comprising (preferably, at least 20, 30, 40, 50, 60, 70, 75, 80, 85, 90, 95, 98, 99, or 100 percent by volume, based on the total metal oxide volume of the particle) eutectic material, wherein the eutectic material comprises eutectic of at least two of (a) crystalline  $\text{Al}_2\text{O}_3$ , (b) crystalline  $\text{Y}_2\text{O}_3$ , (c) a first crystalline, complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , or (d) a second, different (i.e., different than the first crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$ ), crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ . Preferably, a fused, crystalline abrasive particle according to the present invention comprises, on a theoretical oxide basis, at least 30 percent (or even at least 40, 50, 60, 70, or 80 percent) by weight  $\text{Al}_2\text{O}_3$ , based on the total metal oxide content the particle. A preferred eutectic is  $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$  eutectic.

In another aspect, the present invention provides a plurality of particles having a particle size distribution ranging from fine to coarse, wherein at least a portion of the plurality of particles are fused, crystalline abrasive particles according to the present invention.

In this application:

“simple metal oxide” refers to a metal oxide comprised of a one or more of the same metal element and oxygen (e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ , and  $\text{Y}_2\text{O}_3$ );

“complex metal oxide” refers to a metal oxide comprised of two or more different metal elements and oxygen (e.g.,  $\text{CeAl}_{11}\text{O}_{18}$ ,  $\text{Dy}_3\text{Al}_5\text{O}_{12}$ ,  $\text{MgAl}_2\text{O}_4$ , and  $\text{Y}_3\text{Al}_5\text{O}_{12}$ );

“complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$ ” refers to a complex metal oxide comprised of, on a theoretical oxide basis,  $\text{Al}_2\text{O}_3$  and one or more metal elements other than Al (e.g.,  $\text{CeAl}_{11}\text{O}_{18}$ ,  $\text{Dy}_3\text{Al}_5\text{O}_{12}$ ,  $\text{MgAl}_2\text{O}_4$ , and  $\text{Y}_3\text{Al}_5\text{O}_{12}$ );

“complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ ” refers to a complex metal oxide comprised of, on a theoretical oxide basis,  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  (e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ );

“complex  $\text{Al}_2\text{O}_3 \cdot \text{rare earth oxide}$ ” refers to a complex metal oxide comprised of, on a theoretical oxide basis,  $\text{Al}_2\text{O}_3$  and rare earth oxide (e.g.,  $\text{CeAl}_{11}\text{O}_{18}$  and  $\text{Dy}_3\text{Al}_5\text{O}_{12}$ );



“rare earth oxides” refer to, on a theoretical oxide basis,  $\text{CeO}_2$ ,  $\text{Dy}_2\text{O}_3$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Lu}_2\text{O}_3$ ,  $\text{Nd}_2\text{O}_3$ ,  $\text{Pr}_6\text{O}_{11}$ ,  $\text{Sm}_2\text{O}_3$ ,  $\text{Th}_4\text{O}_7$ ,  $\text{Tm}_2\text{O}_3$ , and  $\text{Yb}_2\text{O}_3$ ; and

“particle size” is the longest dimension of a particle.

5 In another aspect, the present invention provides a method for making fused, crystalline abrasive particles according to the present invention, the method comprising:

melting at least one  $\text{Al}_2\text{O}_3$  source and at least one  $\text{Y}_2\text{O}_3$  source to provide a melt; and

10 converting the melt to the fused, crystalline abrasive particles.

Fused abrasive particles according to the present invention can be incorporated into various abrasive products such as coated abrasives, bonded abrasives, nonwoven abrasives, and abrasive brushes.

15 The present invention also provides a method of abrading a surface, the method comprising:

contacting at least one fused abrasive particle according to the present invention (preferably, a plurality of fused abrasive particles according to the present invention) with a surface of a workpiece; and

20 moving at least of one the fused abrasive particle according to the present invention or the surface relative to the other to abrade at least a portion of the surface with the fused abrasive particle according to the present invention.

Preferred fused abrasive particles according to the present invention provide superior grinding performance as compared to conventional fused abrasive particles. Preferred fused abrasive particles according to the present invention are 25 sufficiently microstructurally and chemically stable to allow them to be used with vitrified bonding systems without the significant decrease in abrading performance of conventional fused alumina-zirconia abrasive particles used with vitrified bonding systems.

#### Brief Description of the Drawing

30 FIG. 1 is a fragmentary cross-sectional schematic view of a coated abrasive article including fused abrasive particles according to the present invention;

FIG. 2 is a perspective view of a bonded abrasive article including fused abrasive particles according to the present invention;

FIG. 3 is an enlarged schematic view of a nonwoven abrasive article including fused abrasive particles according to the present invention;

5 FIG. 4 is a schematic of an exemplary portion of interpenetrating phases in a eutectic colony;

FIG. 5 is a Differential thermal analysis (DTA) plot and Thermogravimetric Analysis (TGA) plot of Example 1 fused material;

10 FIG. 6 is a DTA plot and TGA plot of Comparative Example E fused material;

FIG. 7 is a DTA plot and TGA plot of Comparative Example B abrasive particles;

FIG. 8 is a scanning electron photomicrographs of polished cross-sections of Example 1 fused material;

15 FIGS. 9 and 10 are scanning electron photomicrographs of polished cross-sections of Comparative Example D fused material, respectively;

FIG. 11 a scanning electron photomicrograph of a polished cross-section of a Comparative Example B abrasive particle;

20 FIGS. 12 and 13 are scanning electron photomicrographs of polished cross-sections of Comparative Example B abrasive particles after exposure to various heating conditions;

FIG. 14 is a scanning electron photomicrograph of a polished cross-section of Comparative Example B abrasive particles after exposure to vitrified bonding material;

25 FIG. 15 is a scanning electron photomicrograph of a polished cross-section of Comparative Example E material;

FIG. 16 is a scanning electron photomicrograph of a polished cross-section of Comparative Example E material after exposure to a specified heating condition;

30 FIGS. 17 and 18 are scanning electron photomicrographs of polished cross-sections of Example 2 fused materials; and

FIGS. 19, 20, 21, 22, and 23 are scanning electron photomicrographs of polished cross-sections of Example 3, 4, 5, 6, and 7, and fused materials, respectively.

#### Detailed Description

5 Fused abrasive particles according to the present invention can be made by heating the appropriate metal oxides sources to form a melt, preferably a homogenous melt, and then rapidly cooling the melt to provide a solidified mass. The solidified mass is typically crushed to produce the desired particle size distribution of abrasive particles.

10 More specifically, fused abrasive particles according to the present invention can be made by charging a furnace with sources of (on a theoretical oxide basis)  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ , and other optional additives (e.g., other metal oxides and processing aids). The metal oxide sources can be added to the furnace, for example, together and melted, or sequentially and melted.

15 For solidified melt material containing complex metal oxide(s), at least a portion of the metal oxide present in the melted metal oxide sources (i.e., the melt) react to form complex metal oxide(s) during formation process of the solidified material. For example, an  $\text{Al}_2\text{O}_3$  source and a  $\text{Y}_2\text{O}_3$  source may react to form  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (i.e.,  $5\text{Al}_2\text{O}_3 + 3\text{Y}_2\text{O}_3 \rightarrow 2\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $\text{YAlO}_3$  (i.e.,  $\text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3 \rightarrow 2\text{YAlO}_3$ ), or  
20  $\text{Y}_4\text{Al}_2\text{O}_9$  (i.e.,  $\text{Al}_2\text{O}_3 + 2\text{Y}_2\text{O}_3 \rightarrow \text{Y}_4\text{Al}_2\text{O}_9$ ).

Depending upon the relative proportions of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , the resultant solidified material, and ultimately the fused abrasive particles, may comprise:

(a) crystalline  $\text{Al}_2\text{O}_3$  together with crystalline  $\text{Al}_2\text{O}_3$ -complex  
25  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  is, for example,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) eutectic;  
and/or

(b) crystalline  $\text{Al}_2\text{O}_3$ -complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again complex  
 $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  is, for example,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) eutectic; and/or

(c) crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again, complex  
 $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  is, for example,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) together with crystalline  $\text{Al}_2\text{O}_3$ -complex  
30  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  is, for example,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ )  
eutectic.

If  $\text{Al}_2\text{O}_3$  reacts with  $\text{Y}_2\text{O}_3$  to form two complex metal oxides, the resulting solidified material, and ultimately the fused abrasive particles, depending upon the relative proportions of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , may comprise:

- (a) first crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$  or  $\text{YAlO}_3$ ) together with first crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again, e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$  or  $\text{YAlO}_3$ , respectively)-second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (e.g.,  $\text{YAlO}_3$  or  $\text{Y}_4\text{Al}_2\text{O}_9$ , respectively) eutectic;
- (b) first crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again, e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$  or  $\text{YAlO}_3$ )-second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again, e.g.,  $\text{YAlO}_3$  or  $\text{Y}_4\text{Al}_2\text{O}_9$ , respectively) eutectic; and/or
- (c) second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again, e.g.,  $\text{YAlO}_3$  or  $\text{Y}_4\text{Al}_2\text{O}_9$ ) together with first crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again, e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$  or  $\text{YAlO}_3$ )-second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (again, e.g.,  $\text{YAlO}_3$  or  $\text{Y}_4\text{Al}_2\text{O}_9$ , respectively) eutectic.

It is understood, however, the particular phases formed are dependent upon several factors including the melt composition and solidification conditions. Typically it is preferred that the composition of the melt and the solidification conditions are such that a large portion of the resulting solidified material is occupied by eutectic (i.e., the formulation of the solidified material corresponds to close to eutectic proportions of the various metal oxide phases that present in the material). Although not wanting to be bound by theory, some metastable conditions during formation of the solidified material may lead to the formation of alternative eutectic. For example, if under normal, stable conditions the eutectic that forms is  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$ , under some metastable conditions  $\text{Al}_2\text{O}_3/\text{YAlO}_3$  eutectic may form in place of, or in addition to  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$  eutectic.

It is also within the scope of the present invention to substitute a portion of the yttrium and/or aluminum cations in the complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  (e.g., yttrium aluminate exhibiting a garnet crystal structure) with other cations. For example, a portion of the Al cations in a complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  may be substituted with at least one cation of an element selected from the group consisting of: Cr, Ti, Sc, Fe, Mg, Ca, Si, Co, and combinations thereof. For example, a portion of the Y cations in a complex

$\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  may be substituted with at least one cation of an element selected from the group consisting of: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Th, Tm, Yb, Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Mg, Ca, Sr, and combinations thereof. Similarly, it is also with in the scope of the present invention to substitute a portion of the aluminum cations in alumina. For example, Cr, Ti, Sc, Fe, Mg, Ca, Si, and Co can substitute for aluminum in alumina structure. The substitution of cations as described above may affect the properties (e.g. hardness, toughness, strength, thermal conductivity, etc.) of the abrasive particles.

Further, other eutectics will be apparent to those skilled in the art after reviewing the present disclosure. For example, phase diagrams depicting various eutectics are known in the art.

Fused abrasive particles according to the present invention containing eutectic material typically are comprised of eutectic colonies. An individual colony contains generally homogeneous microstructural characteristics (e.g., similar size and orientation of crystals of constituent phases within a colony). Typically, impurities, if present, in the fused, crystalline abrasive particles according to the present invention, tend to segregate to colony boundaries, and may be present alone and/or as reaction products (e.g., as a complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  and/or a complex  $\text{Y}_2\text{O}_3 \cdot \text{metal oxide}$ ) as crystalline and/or amorphous (glass) phase(s).

Examples of eutectic colony constitutions may include: (a) a simple metal oxide (e.g., an  $\text{Al}_2\text{O}_3$  phase) and a complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (e.g., a  $\text{Y}_3\text{Al}_5\text{O}_{12}$  phase), or (b) a two, different complex metal oxides (e.g., a  $\text{YAlO}_3$  phase and a  $\text{Y}_3\text{Al}_5\text{O}_{12}$  phase). Examples of possible eutectics for  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  include  $\text{Al}_2\text{O}_3$ - $\text{Y}_3\text{Al}_5\text{O}_{12}$  eutectic, and  $\text{YAlO}_3$ - $\text{Y}_3\text{Al}_5\text{O}_{12}$  eutectic.

In another aspect, the phases making up the eutectic colonies include (a) single crystals of two different metal oxides (e.g., single crystals of each of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), (b) a single crystal of one metal oxide (e.g., single crystal  $\text{Al}_2\text{O}_3$ ) and a plurality of crystals of a different metal oxide (e.g., polycrystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), or (c) two different polycrystalline metal oxides (e.g., polycrystalline  $\text{Al}_2\text{O}_3$  and polycrystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ).

The colonies may be in any of a variety of shapes, typically, ranging from essentially spherical to columnar. The composition, phase, and/or microstructure (e.g., crystallinity (i.e., single crystal or polycrystalline) and crystal size) of each colony may be the same or different. The orientation of the crystals inside the colonies may vary from one colony to another. The phases making up a eutectic may be present in a variety of shapes such as, for example, rod or platelet-like to "chinese script"-like. Such differences between colonies may even be present between adjacent colonies. The phases making up some eutectic colonies are frequently present as an interpenetrating network(s). For example, referring to FIG. 4, eutectic colony 150 comprises first crystalline metal oxide phase 151 and second crystalline metal oxide phase 153. The two continuous phases form an entangled, three-dimensional network.

The number of colonies, their sizes and compositions are affected, for example, by the melt composition and solidification conditions. Although not wanting to be bound by theory, it is believed that the closer the melt composition is to the exact eutectic composition, the smaller the number of colonies that are formed. In another aspect, however, it is believed that slow, unidirectional solidification of the melt also tends to minimize the number of colonies formed, while multidirectional solidification with relatively higher cooling rates tends to increase the number of colonies formed. The solidification rate (i.e., cooling rate) of the melt and/or multidirectional solidification of the melt tend to affect the type and/or number of microstructural imperfections (e.g., pores) present in the resulting fused abrasive particles. For example, although not wanting to be bound by theory, relatively rapid solidification (i.e., solidification with relatively high cooling rates) and/or multidirectional solidification tend to lead to an increase in the type and/or number of microstructural imperfections (e.g., pores) present in the resulting fused abrasive particles. Relatively slow solidification, however, tends to lead to an increase in the size of the colonies, and/or crystals present in the solidified material; although it may be possible through slow and controlled cooling, for example, to eliminate formation of colonies. Hence, in selecting the cooling rate and/or degree of multidirectional solidification, there may be a need to increase or decrease the cooling rate to obtain the optimal balance of desirable

and undesirable microstructural characteristics associated with the various cooling rates.

Further, for a given composition, the size of the colonies and phases present within the colonies tends to decrease as the cooling rate of the melt increases. Typically, the eutectic colonies in abrasive particles according to the present invention are, on average, less than 100 micrometers, preferably, less than 50 micrometers, wherein such size for a given colony is the average of the two largest dimensions measured from a polished cross-section of the colony, as viewed with a scanning electron microscope (SEM). Typically, the smallest dimension of the crystalline phases making up the eutectic in a colony, as measured from a polished cross-section of the colony viewed with an SEM, is up to 10 micrometers; preferably, up to 5 micrometers; more preferably, up to 1 micrometer, or even up to 0.5 micrometer.

Some abrasive particles according to the present invention also include primary crystals of at least one of the metal oxide phases making up the eutectic constituent of the abrasive particle. For example, if the eutectic portion is made up of a  $\text{Al}_2\text{O}_3$  phase and a complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide}$  (e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) phase, the microstructure may also include primary crystals of  $\text{Al}_2\text{O}_3$  or  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , which is believed to occur when the composition of the melt from which the abrasive particles are formed is rich in  $\text{Al}_2\text{O}_3$  or  $\text{Y}_2\text{O}_3$  (i.e., the melt contains, on a theoretical oxide basis, an excess of  $\text{Al}_2\text{O}_3$  or  $\text{Y}_2\text{O}_3$ , respectively, relative to the eutectic).

The formation of the primary crystals is believed to result from a deviation from the particular eutectic proportions. The greater the deviation, the larger the overall fraction of primary crystals. The primary crystals may be found in a variety of shapes, typically ranging from rod-like structures to dendritic-like structures. Although not wanting to be bound by theory, it is believed that the presence and/or formation of a primary crystal(s) adjacent to a colony may affect the resulting microstructure of the colony. In some cases it may be advantageous (e.g., for increased abrading performance) to have primary crystals (e.g., primary  $\text{Al}_2\text{O}_3$  crystals) present in the abrasive particles. It is also believed, however, that the abrading performance of an abrasive particle tends to decrease as the size of the primary crystals increase.

Further, although not wanting to be bound by theory, it is believed that small additions (e.g., less than 5 percent by weight) of metal oxides other than those making up the eutectic may affect colony boundaries, and in turn affect properties (e.g., hardness and toughness) of the abrasive particle.

5 Sources of (on a theoretical oxide basis)  $\text{Al}_2\text{O}_3$  for making abrasive particles according to the present invention include those known in the art for making conventional fused alumina and alumina-zirconia abrasive particles. Commercially available  $\text{Al}_2\text{O}_3$  sources include bauxite (including both natural occurring bauxite and synthetically produced bauxite), calcined bauxite, hydrated aluminas (e.g., boehmite, 10 and gibbsite), Bayer process alumina, aluminum ore, gamma alumina, alpha alumina, aluminum salts, aluminum nitrates, and combinations thereof. The  $\text{Al}_2\text{O}_3$  source may contain, or only provide,  $\text{Al}_2\text{O}_3$ . Alternatively, the  $\text{Al}_2\text{O}_3$  source may contain, or provide  $\text{Al}_2\text{O}_3$ , as well as one or more metal oxides other than  $\text{Al}_2\text{O}_3$  (including materials of or containing complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxides}$  (e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ )).

15 Commercially available sources of (on a theoretical oxide basis)  $\text{Y}_2\text{O}_3$  for making abrasive particles according to the present invention include yttrium oxide powders, yttrium, yttrium-containing ores, and yttrium salts (e.g., yttrium carbonates, nitrates, chlorides, hydroxides, and combinations thereof). The  $\text{Y}_2\text{O}_3$  source may contain, or only provide,  $\text{Y}_2\text{O}_3$ . Alternatively, the  $\text{Y}_2\text{O}_3$  source may contain, or provide 20  $\text{Y}_2\text{O}_3$ , as well as one or more metal oxides other than  $\text{Y}_2\text{O}_3$  (including materials of or containing complex  $\text{Y}_2\text{O}_3 \cdot \text{metal oxides}$  (e.g.,  $\text{Y}_3\text{Al}_5\text{O}_{12}$ )).

Optionally, fused abrasive particles according to the present invention further comprise other oxide metal oxides (i.e., metal oxides other than  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ ). The addition of certain metal oxides may alter the crystalline structure or 25 microstructure of the resulting fused abrasive particles. For example, although not wishing to be bound by any theory, it is theorized that certain metal oxides or metal oxide containing compounds (even when used in relatively small amounts, for example, even 0.01 to 5 percent by weight, based on the total metal oxide content of the fused abrasive particle) may be present at the boundaries between the eutectic colonies. The 30 presence of these metal oxides, which may be in the form of reaction products together or with the  $\text{Al}_2\text{O}_3$  and/or  $\text{Y}_2\text{O}_3$  may affect the fracture characteristics and/or



microstructure of the fused abrasive particles, and/or may affect the grinding characteristics of the abrasive particles. The optional metal oxides may also act as a processing aid, for example, to increase the density of the fused abrasive particles, by decreasing the size and/or number of pores in the fused abrasive particles. The optional metal oxides may also act as a processing aid, for example, to increase or decrease the effective melting temperature of the melt. Thus certain metal oxides may be added for processing reasons.

Fused abrasive particles according to the present invention typically comprise less than 50 percent by weight (more typically, less than 20 percent by weight; in some cases in the range from 0.01 to 5 percent by weight, in other cases from 0.1 to 1 percent by weight) of metals oxides (on a theoretical oxide basis) other than alumina and yttria, based on the total metal oxide content of the respective abrasive particle. Sources of the other metal oxides are also readily commercially available.

Examples of optional metal oxides include, on a theoretical oxide basis, rare earth oxides, BaO, CaO, Cr<sub>2</sub>O<sub>3</sub>, CoO, Fe<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, Li<sub>2</sub>O, MgO, MnO, NiO, SiO<sub>2</sub>, TiO<sub>2</sub>, Na<sub>2</sub>O, Sc<sub>2</sub>O<sub>3</sub>, SrO, V<sub>2</sub>O<sub>3</sub>, ZnO, ZrO<sub>2</sub>, and combinations thereof. Further with regard to rare earth oxides, commercially available sources of rare earth oxides for making abrasive particles according to the present invention include rare earth oxide powders, rare earth metals, rare earth-containing ores (e.g., bastnasite and monazite), rare earth salts, rare earth nitrates, and rare earth carbonates. The rare earth oxide(s) source may contain, or only provide, rare earth oxide(s). Alternatively, the rare earth oxide(s) source may contain, or provide rare earth oxide(s), as well as one or more metal oxides other than rare earth oxide(s) (including materials of or containing complex rare earth oxide • other metal oxides (e.g., Dy<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>, CeAl<sub>11</sub>O<sub>18</sub>, etc.)).

Metal oxide sources for making abrasive particles according to the present invention also include fused abrasive particles (e.g., fused alumina abrasive particles) or other fused material (e.g., fused alumina material) having the same composition or different composition(s), which together with remaining metal oxide sources, provide the desired composition of the fused abrasive particles.

A reducing agent, such as a carbon source may be added to reduce impurities during the melting process. Examples of carbon sources include: coal,

graphite, petroleum coke, or the like. Typically, the amount of carbon included in the charge to the furnace is up 5% by weight of the charge; more typically, up to 3% by weight, and more typically, up to 2% by weight. Iron may also be added to the furnace charge to aid in the removal of impurities. The iron can combine with the impurities to make a material that can be removed magnetically, for example, from the melt or crushed solidified material.

It is also within the scope of the present invention to include metal borides, carbides, nitrides, and combinations thereof in the fused, crystalline abrasive particles according to the present invention. Such materials may even be present within (e.g., as inclusions) the eutectic material. Examples of metal borides, carbides, and nitrides may include titanium diboride, aluminum carbide, aluminum nitride, titanium carbide, titanium nitride, silicon carbide, boron carbide, and boron nitride. Such materials are known in the art, and are commercially available.

The particular selection of metal oxide sources and other additives for making fused abrasive particles according to the present invention typically takes into account, for example, the desired composition and microstructure of the resulting abrasive particles, the desired physical properties (e.g., hardness or toughness) of the resulting abrasive particles, avoiding or minimizing the presence of undesirable impurities, the desired grinding characteristics of the resulting abrasive particles, and/or the particular process (including equipment and any purification of the raw materials before and/or during fusion and/or solidification) being used to prepare the abrasive particles.

The metal oxide sources and other additives can be in any form suitable to the process and equipment being used to make the abrasive particles. The raw materials can be fused using techniques and equipment known in the art for making conventional fused alumina and alumina-zirconia abrasive particles (see, e.g., U.S. Pat. Nos. 3,781,172 (Pett et al.), 3,891,408 (Rowse et al.), 4,035,162 (Brothers et al.), 4,070,796 (Scott), 4,073,096 (Ueltz et al.), 4,126,429 (Watson), 4,457,767 (Poon et al.), 5,143,522 (Gibson et al.), and Re. 31,128 (Walker et al.)).

Examples of furnaces for melting the metal oxide sources and other additives include arc furnaces, pig furnaces, arc tapping furnaces, electric furnaces,

electric arc furnaces, and gas fired furnaces. Suitable electric furnaces include those in which the electrodes are arranged to create a "kissing arc", wherein the lower tip of the electrodes are not in contact within the molten mass, as well as those in which the electrodes are submerged in the molten mass to provide resistance heating via current  
5 passing through the melt.

The furnace may have a lining (sometimes referred to as a "shell" or "skeleton") that covers the inside of the furnace walls. The lining may be made from a material dissimilar to the fused abrasive particle composition. Typically, however it is preferred that the furnace lining is made from a composition or material similar,  
10 sometimes nearly identical or identical to the composition of the fused abrasive particle. Thus during processing, if the outer (exposed) surface of the lining melts, the potential contamination of the melt is reduced or minimized.

For some metal oxide sources and other additives, it may also be desirable to preheat feed prior to charging it into the furnace, or otherwise combining it  
15 with other metal oxide sources and other additives. For example, if carbonate, nitrate or other salts are used as the metal oxide source, it may be desirable to calcine (e.g., by heating them in air at about 400-1000°C) such materials prior to adding them with the other metal oxide source materials.

Generally, the metal oxide sources and other additives, if present, are  
20 heated to a molten state, and mixed until the melt is homogenous. Typically, the melt is heated to and held at a temperature at least 50°C (preferably, at least 100°C) above the melting point of the melt. If the temperature of the melt is too low, the viscosity of the melt may be undesirably too high, making it more difficult to homogenize the various metal oxide sources and other additives making up the melt, or to pour or otherwise  
25 transfer the melt from the furnace. If the temperature of the melt is too high temperature, and/or the melt heated for too long, energy will be wasted, and there may be undesirable volatilization of components of the melt as well.

In some cases, it may be desirable, to mix, or otherwise blend the metal oxide sources and other additives (e.g., volatile components (e.g., water or organic  
30 solvent) which may assist in forming a homogenous mixture or blend), if present, together prior to forming the melt. For example, particulate metal oxide sources can be

milled (e.g., ball milled) to both mix the materials together, as well as reduce the size of the particulate material. Other techniques for mixing or blending the metal oxide sources and other additives, if present, together prior to forming the melt include high shear mixers, paddle mixers, V-blenders, tumblers, and the like. Milling times may  
5 range from several minutes to several hours, or even days. Optionally, fugitive materials such as water and organic solvents may be removed from the mixture or blend of metal oxide sources and other additives, for example, by heating, prior to forming the melt. For ease of handling, the metal oxide sources and other additives may also be agglomerated prior to charging them to the furnace.

10 The atmosphere over the melt may be at atmospheric pressure, a pressure above atmospheric pressure, or a pressure below atmospheric pressure, although a pressure below atmospheric pressure may be preferred in order to reduce the number of pores in the resulting solidified material. The atmosphere over the melt may also be controlled to provide an oxidizing, reducing, or inert atmosphere which may  
15 affect the melt chemistry.

Reducing conditions during melting may aid in purifying the melt. In addition to, or alternatively to, adding a reducing agent to the melt, suitable reducing conditions may be obtained using carbon electrodes with an electric arc melting furnace. Under suitable reducing conditions, some impurities (e.g., silica, iron oxide,  
20 and titania) will convert to their respective molten metallic form, leading to a higher specific gravity for the melt. Such free metal(s) impurities would then tend to sink to the bottom of the furnace.

In another aspect, it may be desirable to oxidize free metal present in the melt before the melt is cooled (e.g., before pouring the melt from the furnace). For  
25 example, an oxygen lance(s) may be inserted into the melt just prior to pouring the melt from the furnace (see, e.g., U.S. Pat. No. 960,712).

The melt can be cooled using any of a variety of techniques known in the art. Typically the furnace containing the melt is capable of being tilted such that the melt can be poured over or into a heat sink. Examples of heat sinks include metallic  
30 balls (e.g., cast iron or carbon steel balls), metallic rods, metallic plates, metallic rolls, and the like. In some instances, these heat sink materials may be internally cooled (e.g.,

water-cooled or a suitable refrigerant) to achieve fast cooling rates. The heat sink material may also be pieces of pre-fused abrasive particles (having the same or a different composition being solidified) or other refractory material.

Further with regard to heat sinks, the melt can be cooled by pouring the melt over and in between a plurality of metallic balls. The balls typically range in diameter from about 1 to 50 cm, more typically 5 to 25 cm. The melt may also be cooled using book molds. Suitable book molds consist of a plurality of thin plates (e.g., metallic or graphite plates) that are spaced relatively close together. The plates are usually spaced less than 10 cm apart, typically less than 5 cm, and preferably less than 1 cm apart. The melt may also be poured into graphite or cast iron molds to form slabs. It is generally preferred that such "slabs" be relatively thin so as to achieve faster cooling rates.

The cooling rate is believed to affect the microstructure and physical properties of the solidified material, and thus the fused abrasive particles. Preferably, the melt is rapidly cooled as the size of the crystalline phases of the solidified material generally decreases as the cooling rate increase. Preferred cooling rates are at least 500°C/min.; more preferably, at least 1000°C/min; and even more preferably, at least 1500°C/min. The cooling rate may depend upon several factors including the chemistry of the melt, the melting point of the melt, the type of heat sink, and the heat sink material.

Rapid cooling may also be conducted under controlled atmospheres, such as a reducing, neutral, or oxidizing environment to maintain and/or influence the desired crystalline phases, oxidation states, etc. during cooling.

Additional details on cooling a melt can be found, for example, in U.S. Pat. Nos. Re 31,128 (Walker et al.), 3,781,172 (Pett et al.), 4,070,796 (Scott et al.), 4,194,887 (Ueltz et al.), 4,415,510 (Richmond), 4,439,845 (Richmond), and 5,143,522 (Gibson et al.).

The resulting (solidified) fused material(s) is typically larger in size than that desired for the abrasive particle(s). The fused material can be, and typically is, converted into smaller pieces using crushing and/or comminuting techniques known in the art, including roll crushing, canary milling, jaw crushing, hammer milling, ball

milling, jet milling, impact crushing, and the like. In some instances, it is desired to have two or multiple crushing steps. For example, after the molten material is solidified, it may be in the form of a relatively large mass structure (e.g., a diameter greater than 5 cm. The first crushing step may involve crushing these relatively large masses or "chunks" to form smaller pieces. This crushing of these chunks may be accomplished with a hammer mill, impact crusher or jaw crusher. These smaller pieces may then be subsequently crushed to produce the desired particle size distribution. In order to produce the desired particle size distribution (sometimes referred to as grit size or grade), it may be necessary to perform multiple crushing steps. In general the crushing conditions are optimized to achieve the desired particle shape(s) and particle size distribution.

The shape of fused abrasive particles according to the present invention depends, for example, on the composition and/or microstructure of the abrasive particles, the geometry in which it was cooled, and the manner in which the solidified material is crushed (i.e., the crushing technique used). In general, where a "blocky" shape is preferred, more energy may be employed to achieve this shape. Conversely, where a "sharp" shape is preferred, less energy may be employed to achieve this shape. The crushing technique may also be changed to achieve different desired shapes. Alternatively, abrasive particles may be directly formed into desired shapes by pouring or forming the melt into a mold.

The shape of the abrasive particles may be measured by various techniques known in the art, including bulk density and aspect ratio. The larger the abrasive particle size, the higher the bulk density due to the increased mass associated with larger particle sizes. Thus, when comparing bulk densities, the comparison should be made on abrasive particles having essentially the same particle size. In general, the larger the bulk density number, the "blockier" the abrasive particle is considered to be. Conversely the smaller the bulk density number, the "sharper" the abrasive particle is considered to be. Another way to measure sharpness is through an aspect ratio. The aspect ratio of a grade 36 for example, may range from about 1:1 to about 3:1, typically about 1.2:1 to about 2:1.

The bulk density of the abrasive particles can be measured in accordance with ANSI Standard B74.4-1992 (1992). In general, the bulk density is measured by pouring the abrasive particles sample through a funnel so that the abrasive particles traverses through the funnel in a free flowing manner. Immediately underneath the  
5 funnel is a collection device (typically a graduated cylinder). A predetermined volume of abrasive particles are collected and then weighed. The bulk density is calculated in terms of weight/volume.

Abrasive particles according to the present invention can be screened and graded using techniques well known in the art, including the use of industry  
10 recognized grading standards such as ANSI (American National Standard Institute), FEPA (Federation Europeenne des Fabricants de Products Abrasifs), and JIS (Japanese Industrial Standard). Abrasive particles according to the present invention may be used in a wide range of particle sizes, typically ranging in size from about 0.1 to about 5000 micrometers, more typically from about 1 to about 2000 micrometers; preferably from  
15 about 5 to about 1500 micrometers, more preferably from about 100 to about 1500 micrometers.

In a given particle size distribution, there will be a range of particle sizes, from coarse particles fine particles. In the abrasive art this range is sometimes referred to as a "coarse", "control" and "fine" fractions. Abrasive particles graded  
20 according to industry accepted grading standards specify the particle size distribution for each nominal grade within numerical limits. Such industry accepted grading standards include those known as the American National Standards Institute, Inc. (ANSI) standards, Federation of European Producers of Abrasive Products (FEPA) standards, and Japanese Industrial Standard (JIS) standards. ANSI grade designations  
25 (i.e., specified nominal grades) include: ANSI 4, ANSI 6, ANSI 8, ANSI 16, ANSI 24, ANSI 36, ANSI 40, ANSI 50, ANSI 60, ANSI 80, ANSI 100, ANSI 120, ANSI 150, ANSI 180, ANSI 220, ANSI 240, ANSI 280, ANSI 320, ANSI 360, ANSI 400, and ANSI 600. Preferred ANSI grades comprising abrasive particles according to the present invention are ANSI 8-220. FEPA grade designations include P8, P12, P16,  
30 P24, P36, P40, P50, P60, P80, P100, P120, P150, P180, P220, P320, P400, P500, 600, P800, P1000, and P1200. Preferred FEPA grades comprising abrasive particles

according to the present invention are P12-P220. JIS grade designations include JIS8, JIS12, JIS16, JIS24, JIS36, JIS46, JIS54, JIS60, JIS80, JIS100, JIS150, JIS180, JIS220, JIS 240, JIS280, JIS320, JIS360, JIS400, JIS400, JIS600, JIS800, JIS1000, JIS1500, JIS2500, JIS4000, JIS6000, JIS8000, and JIS10,000. Preferred JIS grades comprising  
5 abrasive particles according to the present invention are JIS8-220.

After crushing and screening, there will typically be a multitude of different abrasive particle size distributions or grades. These multitudes of grades may not match a manufacturer's or supplier's needs at that particular time. To minimize inventory, it is possible to recycle the off demand grades back into the molten mass.  
10 This recycling may occur after the crushing step, where the particles are in large chunks or smaller pieces (sometimes referred to as "fines") that have not been screened to a particular distribution. A charge to the furnace for making fused abrasive particles according to the present invention may consist of anywhere from 0 to 100% by weight recycled fused abrasive particles, typically between 0 to 50% by weight.

15 Typically, the true density, sometimes referred to as specific gravity, of fused abrasive particles according to the present invention is typically at least 80% of theoretical density, although abrasive particles with a lower true density may also be useful in abrasive applications. Preferably, the true density of fused abrasive particles according to the present invention is at least 85% of theoretical density, more preferably  
20 at least 90% of theoretical density, and even more preferably at least 95% of theoretical density.

Typically, fused abrasive particles according to the present invention have an average hardness (i.e., resistance to deformation; also referred to as ("microhardness") of at least 11 GPa; preferably, at least 12, 13, or 14 GPa, more  
25 preferably, at least 15 GPa, and even more preferably, at least 16 GPa, at least 17 GPa, or even at least 18 GPa. In another aspect, fused abrasive particles according to the present invention typically have an average toughness (i.e., resistance to fracture) of at least  $2.0 \text{ MPa m}^{1/2}$ ; preferably at least  $2.5 \text{ MPa m}^{1/2}$ , more preferably at least  $3.0 \text{ MPa m}^{1/2}$ , and even more preferably, at least  $3.3 \text{ MPa m}^{1/2}$ , at least  $3.5 \text{ MPa m}^{1/2}$ , or even at  
30 least  $3.8 \text{ MPa m}^{1/2}$ .



It is also within the scope of the present invention to provide a surface coating on the fused abrasive particles. Surface coatings are known, for example, to improve the adhesion between the abrasive particles and the binder material in the abrasive article. Such surface coatings are described, for example, in U.S. Pat. Nos. 5 1,910,444 (Nicholson), 3,041,156 (Rowse et al.), 4,997,461 (Markhoff-Matheny et al.), 5,009,675 (Kunz et al.), 5,042,991 (Kunz et al.), and 5,085,671 (Martin et al.). Further, in some instances, the addition of the coating improves the abrading characteristics of the abrasive particles. In another aspect, the surface coating may improve adhesion between the abrasive particle of the invention and the binder.

10 In another aspect, after abrasive particles according to the present invention are produced, they may be further heat-treated to improve their physical properties and/or grinding performance. This heat-treating process may occur in an oxidizing atmosphere. Typically this heat-treating process occurs at a temperature between about 1100°C to 1600°C, usually between 1200°C to 1400°C. The time may 15 range from about 1 minute to days, usually between about 5 minutes to 1 hour.

Other suitable preparation techniques for making fused abrasive particles according to the present invention may be apparent to those skilled in the art after reviewing the disclosure herein, as well as, for example, applications having U.S. Serial Nos. 09/495,978, 09/496,422, 09/496,638, and 09/496,713, each filed on February 2, 20 2000, and, 09/618,876, 09/618,879, 09/619,106, 09/619,191, 09/619,192, 09/619,215, 09/619,289, 09/619,563, 09/619,729, and 09/619,744, each filed on July 19, 2000.

For some fused abrasive particles according to the present invention, eutectic phases (e.g.,  $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}\text{-ZrO}_2$ ) making up the colonies have a lamellar 25 arrangement where one crystalline phase (e.g., alumina crystals) exhibit a trigonal shape. Further, the orientation of at least a portion adjacent lamellars (i.e. orientation of eutectic crystallization) follows the orientation of the trigonal (-shaped phase) outline at an angle of about 120 degrees. While not wishing to be bounded by theory, it is believed that during crystallization of the melt of a composition at or near ternary 30 eutectic, primary crystals of one phase (e.g., alumina) may crystallize first as a seed in a trigonal shape. The consequent coupled growth of eutectic in the form of lamellar

follows, at least initially, the orientation of the seed. A eutectic colony then includes seeds (e.g., alumina seeds) of the same orientation (or a single seed) together with the eutectic lamellar growth. Further, colony boundaries may not exhibit phase coarsening as has been observed in binary eutectics (manifested by the significant coarsening of crystals of eutectic phases in an immediate vicinity of colony boundary) such as was  
5 observed for Example 1.

Preferred abrasive particles according to the present invention are thermally stable at elevated temperatures, as compared to conventional fused alumina-zirconia materials (including alumina-zirconia abrasive particles available from Norton  
10 Company, Worcester, MA under the trade designation "NORZON"). When alumina-zirconia eutectic abrasive particles available from Norton Company, Worcester, MA under the trade designation "NORZON, are heated in air, for example, to at least about 350°C, typically at least a portion of the zirconia undergoes a tetragonal and/or cubic to monoclinic phase transformation. This phase transformation is usually detrimental to  
15 the structural integrity of the alumina-zirconia material because it involves volume changes to the zirconia crystalline phases. Further, such phase transformations have been observed to occur preferentially at the boundaries of eutectic colonies, which thereby tend to weaken the boundaries, and which in turn tend to lead to significant degradation of mechanical properties (i.e., hardness, strength, etc.) of the material. In  
20 addition, various impurities, which are typically segregated during solidification of the melt into the eutectic colonies boundaries may also undergo volumetric structural changes (e.g., due to oxidation), leading to further degradation of mechanical properties (i.e., hardness, strength, etc.) of the material.

By contrast, preferred abrasive particles according to the present  
25 invention typically do not exhibit phase transformations of the eutectic phases when heated up to 1000°C (in some cases even up to 1400°C) in air, and thus are thermally stable. Although not wishing to be bound by any theory, it is believed that this thermal stability allows such abrasive particle to be incorporated into vitrified bonded abrasives.

The thermal stability of certain preferred abrasive particles according to  
30 the present invention may be measured or illustrated using a variety of different techniques, including: Differential Thermal Analysis (DTA), Thermogravimetric

Analysis (TGA), X-ray diffraction, hardness measurements, microstructure analysis, color change, and interaction with glass bonds. The thermal stability of the abrasive particles may be dependent, for example, upon the composition, particle chemistry, and processing conditions.

5                   In one test for measuring the thermal stability of certain preferred abrasive particles according to the present invention, the average hardness of the abrasive particles is measured before and after being heated in air at 1000°C in air for 4 hours (see Example 1 (below) for a more complete description of the test). Although there may be some degradation of the average microhardness after being heated for 4  
10                   hours in air at 1000°C, the average hardness of preferred abrasive particles according to the present invention after being heated for 4 hours in air at 1000°C are at least 85%, (preferably at least 90%, more preferably at least 95%, and even more preferably, about 100% or more) of the average microhardness of the abrasive particles prior to such heating.

15                   The thermal stability of certain preferred abrasive particles according to the present invention may also be observed using Scanning Electron Microscopy (SEM), wherein the average microstructure (e.g., porosity, crystal structure, colony size and crystal size (eutectic crystals, and primary crystals, if present) and integrity of the abrasive particles is examined before and after being heated at 1000°C in air for 4  
20                   hours. The microstructure of certain preferred abrasive particles according to the present invention are essentially the same before and after being heated at 1000°C in air for 4 hours.

                  Further, the thermal stability of certain preferred abrasive particles according to the present invention may also be illustrated by comparing the color of the  
25                   abrasive particles before and after they are heated at 1000°C in air for 4 hours. The microstructure of certain preferred abrasive particles according to the present invention is essentially the same before and after being heated at 1000°C in air for 4 hours.

                  The thermal stability of certain preferred abrasive particles according to the present invention may also be illustrated by comparing powder XRD result of the  
30                   abrasive particles before and after they are heated at 1000°C in air for 4 hours. As discussed above, when alumina-zirconia eutectic material is heated in air, typically at

least a portion of the zirconia undergoes a tetragonal and/or cubic to monoclinic phase transformation. The effect of this phase transformation is typically significant enough to be observed via powder XRD. By contrast, the eutectic phases of certain preferred abrasive particles according to the present invention do not exhibit such phase transformations when heated to 1000°C in air, hence no such transformation of the eutectic phases will be observed in the XRD results.

Fused abrasive particles according to the present invention can be used in conventional abrasive products, such as coated abrasive products, bonded abrasive products (including vitrified, resinoid, and metal bonded grinding wheels, cutoff wheels, mounted points, and honing stones), nonwoven abrasive products, and abrasive brushes. Typically, abrasive products (i.e., abrasive articles) include binder and abrasive particles, at least a portion of which is fused abrasive particles according to the present invention, secured within the abrasive product by the binder. Methods of making such abrasive products and using abrasive products are well known to those skilled in the art. Furthermore, fused abrasive particles according to the present invention can be used in abrasive applications that utilize loose abrasive particles, such as slurries of abrading compounds (e.g., polishing compounds), milling media, shot blast media, vibratory mill media, and the like.

Coated abrasive products generally include a backing, abrasive particles, and at least one binder to hold the abrasive particles onto the backing. The backing can be any suitable material, including cloth, polymeric film, fibre, nonwoven webs, paper, combinations thereof, and treated versions thereof. The binder can be any suitable binder, including an inorganic or organic binder (including thermally curable resins and radiation curable resins). The abrasive particles can be present in one layer or in two layers of the coated abrasive product.

An example of a coated abrasive product is depicted in FIG. 1. Referring to this figure, coated abrasive product 1 has a backing (substrate) 2 and abrasive layer 3. Abrasive layer 3 includes fused abrasive particles according to the present invention 4 secured to a major surface of backing 2 by make coat 5 and size coat 6. In some instances, a supersize coat (not shown) is used.

Bonded abrasive products typically include a shaped mass of abrasive particles held together by an organic, metallic, or vitrified binder. Such shaped mass can be, for example, in the form of a wheel, such as a grinding wheel or cutoff wheel. The diameter of grinding wheels typically is about 1 cm to over 1 meter; the diameter of cut off wheels about 1 cm to over 80 cm (more typically 3 cm to about 50 cm). The cut off wheel thickness is typically about 0.5 mm to about 5 cm, more typically about 0.5 mm to about 2 cm. The shaped mass can also be in the form, for example, of a honing stone, segment, mounted point, disc (e.g. double disc grinder) or other conventional bonded abrasive shape. Bonded abrasive products typically comprise about 3-50% by volume bond material, about 30-90% by volume abrasive particles (or abrasive particle blends), up to 50% by volume additives (including grinding aids), and up to 70% by volume pores, based on the total volume of the bonded abrasive product.

A preferred form is a grinding wheel. Referring to FIG. 2, grinding wheel 10 is depicted, which includes fused abrasive particles according to the present invention 11, molded in a wheel and mounted on hub 12.

Nonwoven abrasive products typically include an open porous lofty polymer filament structure having fused abrasive particles according to the present invention distributed throughout the structure and adherently bonded therein by an organic binder. Examples of filaments include polyester fibers, polyamide fibers, and polyaramid fibers. In FIG. 3, a schematic depiction, enlarged about 100x, of a typical nonwoven abrasive product is provided. Such a nonwoven abrasive product comprises fibrous mat 50 as a substrate, onto which fused abrasive particles according to the present invention 52 are adhered by binder 54.

Useful abrasive brushes include those having a plurality of bristles unitary with a backing (see, e.g., U.S. Pat. Nos. 5,427,595 (Pihl et al.), 5,443,906 (Pihl et al.), 5,679,067 (Johnson et al.), and 5,903,951 (Ionta et al.)). Preferably, such brushes are made by injection molding a mixture of polymer and abrasive particles.

Suitable organic binders for making abrasive products include thermosetting organic polymers. Examples of suitable thermosetting organic polymers include phenolic resins, urea-formaldehyde resins, melamine-formaldehyde resins, urethane resins, acrylate resins, polyester resins, aminoplast resins having pendant

$\alpha,\beta$ -unsaturated carbonyl groups, epoxy resins, acrylated urethane, acrylated epoxies, and combinations thereof. The binder and/or abrasive product may also include additives such as fibers, lubricants, wetting agents, thixotropic materials, surfactants, pigments, dyes, antistatic agents (e.g., carbon black, vanadium oxide, graphite, etc.),  
5 coupling agents (e.g., silanes, titanates, zircoaluminates, etc.), plasticizers, suspending agents, and the like. The amounts of these optional additives are selected to provide the desired properties. The coupling agents can improve adhesion to the abrasive particles and/or filler. The binder chemistry may thermally cured, radiation cured or combinations thereof. Additional details on binder chemistry may be found in U.S. Pat.  
10 Nos. 4,588,419 (Caul et al.), 4,751,137 (Tumey et al.), and 5,436,063 (Follett et al.).

More specifically with regard to vitrified bonded abrasives, vitreous bonding materials, which exhibit an amorphous structure and are typically hard, are well known in the art. In some cases, the vitreous bonding material includes crystalline phases. Bonded, vitrified abrasive products according to the present invention may be  
15 in the shape of a wheel (including cut off wheels), honing stone, mounted pointed or other conventional bonded abrasive shape. A preferred vitrified bonded abrasive product according to the present invention is a grinding wheel.

Examples of metal oxides that are used to form vitreous bonding materials include: silica, silicates, alumina, soda, calcia, potassia, titania, iron oxide,  
20 zinc oxide, lithium oxide, magnesia, boria, aluminum silicate, borosilicate glass, lithium aluminum silicate, combinations thereof, and the like. Typically, vitreous bonding materials can be formed from composition comprising from 10 to 100% glass frit, although more typically the composition comprises 20% to 80% glass frit, or 30% to 70% glass frit. The remaining portion of the vitreous bonding material can be a non-  
25 frit material. Alternatively, the vitreous bond may be derived from a non-frit containing composition. Vitreous bonding materials are typically matured at a temperature(s) in the range from about 700°C to about 1500°C, usually in the range from about 800°C to about 1300°C, sometimes in the range from about 900°C to about 1200°C, or even in the range from about 950°C to about 1100°C. The actual temperature at which the bond  
30 is matured depends, for example, on the particular bond chemistry.

Preferred vitrified bonding materials may include those comprising silica, alumina (preferably, at least 10 percent by weight alumina), and boria (preferably, at least 10 percent by weight boria). In most cases the vitrified bonding material further comprise alkali metal oxide(s) (e.g.,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) (in some cases at least 10 percent by weight alkali metal oxide(s)).

Binder materials may also contain filler materials or grinding aids, typically in the form of a particulate material. Typically, the particulate materials are inorganic materials. Examples of useful fillers for this invention include: metal carbonates (e.g., calcium carbonate (e.g., chalk, calcite, marl, travertine, marble, and limestone), calcium magnesium carbonate, sodium carbonate, magnesium carbonate), silica (e.g., quartz, glass beads, glass bubbles and glass fibers) silicates (e.g., talc, clays, (montmorillonite) feldspar, mica, calcium silicate, calcium metasilicate, sodium aluminosilicate, sodium silicate) metal sulfates (e.g., calcium sulfate, barium sulfate, sodium sulfate, aluminum sodium sulfate, aluminum sulfate), gypsum, vermiculite, wood flour, aluminum trihydrate, carbon black, metal oxides (e.g., calcium oxide (lime), aluminum oxide, titanium dioxide), and metal sulfites (e.g., calcium sulfite).

In general, the addition of a grinding aid increases the useful life of the abrasive product. A grinding aid is a material that has a significant effect on the chemical and physical processes of abrading, which results in improved performance. Although not wanting to be bound by theory, it is believed that a grinding aid(s) will (a) decrease the friction between the abrasive particles and the workpiece being abraded, (b) prevent the abrasive particles from "capping" (i.e., prevent metal particles from becoming welded to the tops of the abrasive particles), or at least reduce the tendency of abrasive particles to cap, (c) decrease the interface temperature between the abrasive particles and the workpiece, and/or (d) decreases the grinding forces.

Grinding aids encompass a wide variety of different materials and can be inorganic or organic based. Examples of chemical groups of grinding aids include waxes, organic halide compounds, halide salts and metals and their alloys. The organic halide compounds will typically break down during abrading and release a halogen acid or a gaseous halide compound. Examples of such materials include chlorinated waxes like tetrachloronaphtalene, pentachloronaphtalene, and polyvinyl chloride. Examples

of halide salts include sodium chloride, potassium cryolite, sodium cryolite, ammonium cryolite, potassium tetrafluoroborate, sodium tetrafluoroborate, silicon fluorides, potassium chloride, and magnesium chloride. Examples of metals include, tin, lead, bismuth, cobalt, antimony, cadmium, and iron titanium. Other miscellaneous grinding  
5 aids include sulfur, organic sulfur compounds, graphite, and metallic sulfides. It is also within the scope of the present invention to use a combination of different grinding aids, and in some instances this may produce a synergistic effect. The preferred grinding aid is cryolite; the most preferred grinding aid is potassium tetrafluoroborate.

Grinding aids can be particularly useful in coated abrasive and bonded  
10 abrasive products. In coated abrasive products, grinding aid is typically used in the supersize coat, which is applied over the surface of the abrasive particles. Sometimes, however, the grinding aid is added to the size coat. Typically, the amount of grinding aid incorporated into coated abrasive products are about 50-300 g/m<sup>2</sup> (preferably, about 80-160 g/m<sup>2</sup>). In vitrified bonded abrasive products grinding aid is typically  
15 impregnated into the pores of the product.

The abrasive products can contain 100% fused abrasive particles according to the present invention, or blends of such abrasive particles with other abrasive particles and/or diluent particles. However, at least about 2% by weight, preferably at least about 5% by weight, and more preferably about 30-100% by weight,  
20 of the abrasive particles in the abrasive products should be abrasive particles according to the present invention. In some instances, the abrasive particles according the present invention may be blended with another abrasive particles and/or diluent particles at a ratio between 5 to 75% by weight, about 25 to 75% by weight, about 40 to 60% by weight, or about 50% to 50% by weight (i.e., in equal amounts by weight). Examples of  
25 suitable conventional abrasive particles include fused aluminum oxide (including white fused alumina, heat-treated aluminum oxide and brown aluminum oxide), silicon carbide, boron carbide, titanium carbide, diamond, cubic boron nitride, garnet, fused alumina-zirconia, and sol-gel-derived abrasive particles, and the like. The sol-gel-derived abrasive particles may be seeded or non-seeded. Likewise, the sol-gel-derived  
30 abrasive particles may be randomly shaped or have a shape associated with them, such as a rod or a triangle. Examples of sol gel abrasive particles include those described



U.S. Pat. Nos. 4,314,827 (Leitheiser et al.), 4,518,397 (Leitheiser et al.), 4,623,364 (Cottringer et al.), 4,744,802 (Schwabel), 4,770,671 (Monroe et al.), 4,881,951 (Wood et al.), 5,011,508 (Wald et al.), 5,090,968 (Pellow), 5,139,978 (Wood), 5,201,916 (Berg et al.), 5,227,104 (Bauer), 5,366,523 (Rowenhorst et al.), 5,429,647 (Larmie), 5,498,269 (Larmie), and 5,551,963 (Larmie). Additional details concerning sintered alumina abrasive particles made by using alumina powders as a raw material source can also be found, for example, in U.S. Pat. Nos. 5,259,147 (Falz), 5,593,467 (Monroe), and 5,665,127 (Moltgen). In some instances, blends of abrasive particles may result in an abrasive article that exhibits improved grinding performance in comparison with abrasive articles comprising 100% of either type of abrasive particle.

If there is a blend of abrasive particles, the abrasive particle types forming the blend may be of the same size. Alternatively, the abrasive particle types may be of different particle sizes. For example, the larger sized abrasive particles may be abrasive particles according to the present invention, with the smaller sized particles being another abrasive particle type. Conversely, for example, the smaller sized abrasive particles may be abrasive particles according to the present invention, with the larger sized particles being another abrasive particle type.

Examples of suitable diluent particles include marble, gypsum, flint, silica, iron oxide, aluminum silicate, glass (including glass bubbles and glass beads), alumina bubbles, alumina beads and diluent agglomerates. Fused abrasive particles according to the present invention can also be combined in or with abrasive agglomerates. Abrasive agglomerate particles typically comprise a plurality of abrasive particles, a binder, and optional additives. The binder may be organic and/or inorganic. Abrasive agglomerates may be randomly shape or have a predetermined shape associated with them. The shape may be a block, cylinder, pyramid, coin, square, or the like. Abrasive agglomerate particles typically have particle sizes ranging from about 100 to about 5000 micrometers, typically about 250 to about 2500 micrometers. Additional details regarding abrasive agglomerate particles may be found, for example, in U.S. Pat. Nos. 4,311,489 (Kressner), 4,652,275 (Bloecher et al.), 4,799,939 (Bloecher et al.), 5,549,962 (Holmes et al.), and 5,975,988 (Christianson).

The abrasive particles may be uniformly distributed in the abrasive article or concentrated in selected areas or portions of the abrasive article. For example, in a coated abrasive, there may be two layers of abrasive particles. The first layer comprises abrasive particles other than abrasive particles according to the present invention, and the second (outermost) layer comprises abrasive particles according to the present invention. Likewise in a bonded abrasive, there may be two distinct sections of the grinding wheel. The outermost section may comprise abrasive particles according to the present invention, whereas the innermost section does not. Alternatively, abrasive particles according to the present invention may be uniformly distributed throughout the bonded abrasive article.

Further details regarding coated abrasive products can be found, for example, in U.S. Pat. Nos. 4,734,104 (Broberg), 4,737,163 (Larkey), 5,203,884 (Buchanan et al.), 5,152,917 (Pieper et al.), 5,378,251 (Culler et al.), 5,417,726 (Stout et al.), 5,436,063 (Follett et al.), 5,496,386 (Broberg et al.), 5,609,706 (Benedict et al.), 5,520,711 (Helmin), 5,954,844 (Law et al.), 5,961,674 (Gagliardi et al.), and 5,975,988 (Christinason). Further details regarding bonded abrasive products can be found, for example, in U.S. Pat. Nos. 4,543,107 (Rue), 4,741,743 (Narayanan et al.), 4,800,685 (Haynes et al.), 4,898,597 (Hay et al.), 4,997,461 (Markhoff-Matheny et al.), 5,038,453 (Narayanan et al.), 5,110,332 (Narayanan et al.), and 5,863,308 (Qi et al.). Further details regarding vitreous bonded abrasives can be found, for example, in U.S. Pat. Nos. 4,543,107 (Rue), 4,898,597 (Hay), 4,997,461 (Markhoff-Matheny et al.), 5,094,672 (Giles et al.), 5,118,326 (Sheldon et al.), 5,131,926 (Sheldon et al.), 5,203,886 (Sheldon et al.), 5,282,875 (Wood et al.), 5,738,696 (Wu et al.), and 5,863,308 (Qi). Further details regarding nonwoven abrasive products can be found, for example, in U.S. Pat. No. 2,958,593 (Hoover et al.).

Methods for abrading with abrasive particles according to the present invention range from snagging (i.e., high pressure high stock removal) to polishing (e.g., polishing medical implants with coated abrasive belts), wherein the latter is typically done with finer grades (e.g., less ANSI 220 and finer) of abrasive particles. The abrasive particle may also be used in precision abrading applications, such as

grinding cam shafts with vitrified bonded wheels. The size of the abrasive particles used for a particular abrading application will be apparent to those skilled in the art.

Abrading with abrasive particles according to the present invention may be done dry or wet. For wet abrading, the liquid may be introduced supplied in the  
5 form of a light mist to complete flood. Examples of commonly used liquids include: water, water-soluble oil, organic lubricant, and emulsions. The liquid may serve to reduce the heat associated with abrading and/or act as a lubricant. The liquid may contain minor amounts of additives such as bactericide, antifoaming agents, and the like.

10 Abrasive particles according to the present invention may be used to abrade workpieces such as aluminum metal, carbon steels, mild steels, tool steels, stainless steel, hardened steel, titanium, glass, ceramics, wood, wood-like materials, paint, painted surfaces, organic coated surfaces and the like. The applied force during abrading typically ranges from about 1 to about 100 kilograms.

15

#### Examples

This invention is further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. Various  
20 modifications and alterations of the present invention will become apparent to those skilled in the art. All parts and percentages are by weight unless otherwise indicated.

#### Example 1

A polyethylene bottle was charged with 187.2 grams of alumina powder  
25 (obtained under the trade designation "APA-0.5" from Condea Vista, Tucson, AZ), 112.9 grams of yttrium oxide powder (obtained from H.C. Starck, Newton, MA), 0.6 gram of a dispersing agent (obtained under the trade designation "DURAMAX D-30005" from Rohm and Haas Company, Dear Park, TX), and 100.4 grams of distilled water. The powders were present in amounts to provide 78.6 mole %  $\text{Al}_2\text{O}_3$  and 21.4  
30 mole %  $\text{Y}_2\text{O}_3$ . About 450 grams of alumina milling media (10 mm diameter; 99.9% alumina; obtained from Union Process, Akron, OH) were added to the bottle, and the

mixture was milled for 4 hours to thoroughly mix the ingredients. After the milling, the milling media were removed and the slurry was poured onto a glass ("PYREX") pan where it was dried using a heat-gun held approximately 46 cm (18 inches) above the pan. The pan was slowly oscillated while drying to prevent the settling of the powder  
5 prior to complete drying. After drying with the heat-gun, the pan was placed in a drying oven for an additional 30 minutes at 90°C to more completely dry the material. The dried powder bed was then scored with a spatula and scraped from the pan to form small flakes of material. Each flake weighed about 0.5 to 3 grams. The flakes were calcined in air by heating them to 670°C at rate of about 1°C/min, and then holding  
10 them at 670°C for 1 hour, after which the power to the furnace power was shut-off, and the furnace allowed to cool back to room temperature.

Several of the calcined flakes were melted in an arc discharge furnace (Model No. 1-VAMF-20-22-45; from Advanced Vacuum Systems, Ayer, MA). About 15 grams of the calcined flakes were placed on the chilled copper plate located inside a  
15 furnace chamber. The furnace chamber was evacuated and then backfilled with Argon gas at a 260 torr pressure. An arc was struck between an electrode and a plate. The temperatures generated by the arc discharge were high enough to quickly melt the calcined flakes. After melting was complete, the material was maintained in a molten state for about 30 seconds to homogenize the melt. The resultant melt was rapidly  
20 cooled by shutting off the arc and allowing the melt to cool on its own. Rapid cooling was ensured by small mass of a sample and a large heat sinking capability of a chilled copper plate. The fused material was removed from the furnace within one minute after the power to the furnace was turned off. Although not wanting to be bound by theory, it is estimated that the cooling rate of the melt on the surface of the water chilled copper  
25 plate was 1500°C/min. The fused material was white-green in color.

FIG. 8 is a scanning electron microscope (SEM) photomicrograph of a polished section of fused Example 1 material. The polished section was prepared using conventional mounting and polishing techniques. Polishing was done using a polisher (obtained from Buehler of Lake Bluff, IL under the trade designation "ECOMET 3  
30 TYPE POLISHER-GRINDER"). The sample was polished for about 3 minutes with a diamond wheel, followed by three minutes of polishing with each of 45, 30, 15, 9, and

3 micrometer diamond slurries. The polished sample was coated with a thin layer of gold-palladium and viewed using JEOL SEM (Model JSM 840A). Referring again to FIG. 8, the photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 10-40 micrometers in size. Based on powder x-ray diffraction of a portion of Example 1 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline  $Y_3Al_5O_{12}$ , and the dark portions  $\alpha$ - $Al_2O_3$ . The widths of these phases observed in the polished section were up to about 1 micrometer.

Example 1 fused material was crushed by using a "Chipmunk" jaw crusher (Type VD, manufactured by BICO Inc., Burbank, CA) into (abrasive) particles and graded to retain the -25+30 and -30+35 mesh fractions (USA Standard Testing Sieves). These two mesh fractions were combined to provide a 50/50 blend. Thirty grams of the 50/50 blend of -25+30 and -30+35 mesh fractions were incorporated into a coated abrasive disc. The coated abrasive disc was made according to conventional procedures. The fused abrasive particles were bonded to 17.8 cm diameter, 0.8 mm thick vulcanized fiber backings (having a 2.2 cm diameter center hole) using a conventional calcium carbonate-filled phenolic make resin (48% resole phenolic resin, 52% calcium carbonate, diluted to 81% solids with water and glycol ether) and a conventional cryolite-filled phenolic size resin (32% resole phenolic resin, 2% iron oxide, 66% cryolite, diluted to 78% solids with water and glycol ether). The wet make resin weight was about  $185 \text{ g/m}^2$ . Immediately after the make coat was applied, the fused abrasive particles were electrostatically coated. The make resin was precured for 120 minutes at  $88^\circ\text{C}$ . Then the cryolite-filled phenolic size coat was coated over the make coat and abrasive particles. The wet size weight was about  $850 \text{ g/m}^2$ . The size resin was cured for 12 hours at  $99^\circ\text{C}$ . The coated abrasive disc was flexed prior to testing.

The average microhardnesses of Example 1 abrasive particles were measured by mounting loose abrasive particles (about 10 mesh in size) in mounting resin (obtained under the trade designation "EPOMET" from Buehler Ltd., Lake Bluff, IL). The resulting cylinder of resin was about 2.5 cm (1 inch) in diameter and about 1.9

cm (0.75 inch) tall. The mounted samples were polished using a conventional grinder/polisher (obtained under the trade designation "EPOMET" from Buehler Ltd.) and conventional diamond slurries with the final polishing step using a 1 micrometer diamond slurry (obtained under the trade designation "METADI" from Buehler Ltd.) to  
5 obtain polished cross-sections of the sample.

The microhardness measurements were made using a conventional microhardness tester (obtained under the trade designation "MITUTOYO MVK-VL" from Mitutoyo Corporation, Tokyo, Japan) fitted with a Vickers indenter using a 500-gram indent load. The microhardness measurements were made according to the  
10 guidelines stated in ASTM Test Method E384 Test Methods for Microhardness of Materials (1991). The microhardness values were an average of 20 measurements.. The average microhardness was 16.2 GPa.

Several Example 1 abrasive particles were heated placed in a platinum crucible and heated to 1000°C at 50°C/hour, held at 1000°C for 4 hours (in air), and  
15 then cooled to room temperature at about 100°C/hour. The color of the abrasive particles after heating was the same as before heating (i.e., white-green). The average microhardness of the abrasive particles after heating was 16.1 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed after heating was  
20 substantially the same as the microstructure observed before heating.

Several Example 1 abrasive particles were also heated placed in a platinum crucible and heated to 1000°C at 50°C/hour, held at 1000°C for 8 hours (in air), and then cooled to room temperature at about 100°C/hour. The color of the  
25 abrasive particles after heating was the same as before heating (i.e., white-green). The average microhardness of the abrasive particles after heating was 16.0 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed after heating was substantially the same as the microstructure observed before heating.

### Comparative Example A

The Comparative Example A coated abrasive disc was prepared as described in Example 1 except heat-treated fused alumina abrasive particles (obtained under the trade designation "ALODUR BFRPL"™ from Triebacher, Villach, Austria) was used in place of the Example 1 fused abrasive particles.

### Comparative Example B

The Comparative Example B coated abrasive disc was prepared as described in Example 1 except alumina-zirconia abrasive particles (having a eutectic composition of 53 %  $\text{Al}_2\text{O}_3$  and 47 %  $\text{ZrO}_2$ ; obtained under the trade designation "NORZON" from Norton Company, Worcester, MA) was used in place of the Example 1 fused abrasive particles.

The average microhardness of Comparative Example B abrasive particles was determined, as described above in Example 1, to be 16.0 GPa. The color of the Comparative Example B abrasive particles was gray-navy blue.

Several Comparative Example B abrasive particles were heated placed in a platinum crucible and heated to 1000°C at 50°C/hour, held at 1000°C for 4 hours (in air), and then cooled to room temperature at about 100°C/hour. The color of the abrasive particles after heating was beige. The average microhardness of the abrasive particles after heating was 12.9 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. An SEM photomicrograph a Comparative Example B abrasive particle before heating is shown in FIG. 11. An SEM photomicrograph a Comparative Example B abrasive particle after heating is shown in FIG. 12. The microstructure observed after heating was different than that observed before heating. The differences were observed most predominately at the colony boundaries.

Further powder x-ray diffraction (using a Phillips XRG 3100 x-ray diffractometer with copper K  $\alpha_1$  radiation of 1.54050 Angstrom) was used to qualitatively measure the phases present in Comparative Example B abrasive particles before and after the above described heat-treatment by comparing the peak intensities of 111 of cubic and/or tetragonal reflection at about  $2\theta=30$  degrees, to that of  $11\bar{1}$  of

monoclinic reflection at about  $2\theta=28$  degrees. For reference see "Phase Analysis in Zirconia Systems," Garvie, R. C. and Nicholson, P. S., Journal of the American Ceramic Society, vol 55 (6), pp. 303-305, 1972. The samples were ground and -120 mesh powders used for analysis. The unheat-treated Comparative Example B abrasive particles contained both the monoclinic and cubic and/or tetragonal zirconia phases. For the heat-treated sample, a decrease in the cubic and/or tetragonal phase content with a corresponding increase in monoclinic phase content was observed.

Several Comparative Example B abrasive particles were heated placed in a platinum crucible and heated to 1000°C at 50°C/hour, held at 1000°C for 8 hours (in air), and then cooled to room temperature at about 100°C/hour. The color of the abrasive particles after heating was beige. The average microhardness of the abrasive particles after heating was 12.8 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. An SEM photomicrograph a Comparative Example B abrasive particle after heating is shown in FIG. 13. The microstructure observed after heating was different than that observed before heating. The differences, which were greater than those observed for the heat-treatment at 1000°C for 4 hours, were again observed most predominately at the colony boundaries.

The effect of two vitrified bonding materials on Comparative Example B abrasive particles were evaluated as follows. A first vitrified bond material was prepared by charging a plastic jar (4 3/8 inches (11.1 cm) in diameter; 4 3/8 inches (11.1 cm) in height) with 70 parts of a glass frit (37.9% SiO<sub>2</sub>, 28.5% B<sub>2</sub>O<sub>3</sub>, 15.6% Al<sub>2</sub>O<sub>3</sub>, 13.9% Na<sub>2</sub>O, and 4.1% K<sub>2</sub>O; obtained under the trade designation "FERRO FRIT 3227" from Ferro Corporation, Cleveland, OH), 27 parts of Kentucky Ball Clay (No 6DC; obtained from Old Hickory Clay Company, Hickory, KY), 3.5 parts of Li<sub>2</sub>CO<sub>3</sub> (obtained from Alfa Aesar Chemical Company, Ward Hill, MA), 3 parts CaSiO<sub>3</sub> (obtained from Alfa Aesar Chemical Company), and 625 grams of 1.3 cm (0.5 inch) diameter plastic coated steel media, and then dry milling the contents at 90 rpm for 7 hours. The composition was formulated to provide a vitrified bond material comprising about 45% SiO<sub>2</sub>, about 19% Al<sub>2</sub>O<sub>3</sub>, about 20 % B<sub>2</sub>O<sub>3</sub>, about 10% Na<sub>2</sub>O, about 3% K<sub>2</sub>O, about 1.5% Li<sub>2</sub>O, and about 1.5% CaO. The dry milled material and



Comparative Example B abrasive particles were pressed into a 3.2 cm x 0.6 cm (1.25 inch x 0.25 inch) pellet. The pellet was heated to 1000°C at 50°C/hour, held at 1000°C for 8 hours (in air), and then cooled to room temperature at about 100°C/hour. The pellet was prepared by mixing, in order, 20 parts of Comparative Example B abrasive particles (-20+30 mesh), 0.24 part of hydrolyzed starch (obtained under the trade designation "DEXTRIN" from Aldrich Chemical Company, Milwaukee, WI), 0.02 part glycerine (obtained from Aldrich Chemical Company), 0.72 part water, 3.14 parts of the dry milled material, and 0.4 part of hydrolyzed starch ("DEXTRIN"). The pellet was pressed under a load of 2273 kilograms (5000 lbs.). The average microhardness of the abrasive particles after heating in the vitrified bonding material was 13.6 GPa, although some of the Comparative Example B abrasive particles exhibit such severe degradation that microhardness measurements could not be effectively made (portions of the particles were too weak). There was variability in the color of the heat-treated abrasive particles, although the majority of the particles were beige. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. An SEM photomicrograph of a Comparative Example B abrasive particle after heating is shown in FIG. 14. The microstructure observed after heating was different than that observed before heating. The differences, which were greater than those observed for the heat-treatment at 1000°C for 4 hours, were again observed most predominately at the colony boundaries.

A second vitrified bond material was prepared by charging a plastic jar (4 3/8 inches (11.1 cm) in diameter; 4 3/8 inches (11.1 cm) in height) with 45 parts of Kentucky Ball Clay (No. 6DC; obtained from Old Hickory Clay Company), 28 parts of anhydrous sodium tetraborate (obtained from Alfa Aesar Chemical Company), 25 parts of feldspar (obtained under the trade designation "G-200 Feldspar" from Feldspar Corporation, Atlanta, GA), 3.5 parts of  $\text{Li}_2\text{CO}_3$  (obtained from Alfa Aesar Chemical Company), 2.5 parts of  $\text{CaSiO}_3$  (obtained from Alfa Aesar Chemical Company), and 625 grams of 1.3 cm (0.5 inch) diameter plastic coated steel media, and then dry milling the contents at 90 rpm for 7 hours. The composition was formulated to provide a vitrified bond material comprising about 45%  $\text{SiO}_2$ , about 19%  $\text{Al}_2\text{O}_3$ , about 20 %  $\text{B}_2\text{O}_3$ , about 10%  $\text{Na}_2\text{O}$ , about 3%  $\text{K}_2\text{O}$ , about 1.5%  $\text{Li}_2\text{O}$ , and about 1.5%  $\text{CaO}$ . The

dry milled material and Comparative Example B abrasive particles were pressed into a 3.2 cm x 0.6 cm (1.25 inch x 0.25 inch) pellet. The pellet was heated to 1000°C at 50°C/hour, held at 1000°C for 8 hours (in air), and then cooled to room temperature at about 100°C/hour. The pellet was prepared by mixing, in order, 20 parts of Comparative Example B abrasive particles (-20+30 mesh), 0.24 part of hydrolyzed starch ("DEXTRIN"), 0.02 part glycerine (obtained from Aldrich Chemical Company), 0.72 part water, 3.14 parts of the dry milled material, and 0.4 part of hydrolyzed starch ("DEXTRIN"). The pellet was pressed under a load of 2273 kilograms (5000 lbs.). The average microhardness of the abrasive particles after heating in the vitrified bonding material was 13.4 GPa, although some of the Comparative Example B abrasive particles exhibit such severe degradation that microhardness measurements could not be effectively made (portions of the particles were too weak). There was variability in the color of the heat-treated abrasive particles, although the majority of the particles were beige. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed after heating was different than that observed before heating. The differences, which were greater than those observed for the heat-treatment at 1000°C for 4 hours, were again observed most predominately at the colony boundaries.

#### 20 Comparative Example C

The Comparative Example C coated abrasive disc was prepared as described in Example 1 except sol-gel-derived abrasive particles (commercially available under the trade designation "321 CUBITRON" from the 3M Company, St. Paul, MN) was used in place of the Example 1 fused abrasive particles.

#### 25 Grinding Performance of Example 1 and Comparative Examples A-C

The grinding performance of Example 1 and Comparative Examples A-C coated abrasive discs were evaluated as follows. Each coated abrasive disc was mounted on a beveled aluminum back-up pad, and used to grind the face of a pre-weighed 1.25 cm x 18 cm x 10 cm 1018 mild steel workpiece. The disc was driven at 5,000 rpm while the portion of the disc overlaying the beveled edge of the back-up pad

contacted the workpiece at a load of 8.6 kilograms. Each disc was used to grind individual workpiece in sequence for one-minute intervals. The total cut was the sum of the amount of material removed from the workpieces throughout the test period. The total cut by each sample after 12 minutes of grinding as well as the cut at 12th minute (i.e., the final cut) are reported in Table 1, below.

Table 1		
Example	Total cut, g	Final cut, g
Comp. A	418	23
Comp. B	621	48
Comp. C	859	75
1	732	56

#### Comparative Example 2

Comparative Example D fused material and abrasive particles were prepared as described in Example 1, except (a) the polyethylene bottle was charged with 173 grams of alumina powder ("APA-0.5"), 19.3 grams of magnesium oxide powder (obtained under the trade designation "MAGCHEM 10-325" from Martin Marietta Magnesia Specialties, Hunt Valley, MD), 107.8 grams of yttrium oxide powder obtained from H.C. Starck, Newton, MA), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 137.4 grams of distilled water, and (b) the powders were present in amounts to provide 64 mole %  $\text{Al}_2\text{O}_3$ , 18 mole %  $\text{MgO}$ , and 18 mole %  $\text{Y}_2\text{O}_3$ . The fused material was white in color.

FIG. 9 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Example 1) of fused Comparative Example D material. The photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies are about 10-40 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example D material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and the dark portions a crystalline  $\text{Al}_2\text{O}_3$ -rich spinel solid solution phase. The width of these phases observed in the polished section were up to about 2 micrometers.

Comparative Example E

Comparative Example E fused material and abrasive particles were prepared as described in Example 1, except (a) the polyethylene bottle was charged with 149.5 grams of alumina powder ("APA-0.5"), 149.4 grams of yttria-stabilized zirconia oxide powder (with a nominal composition of 94 wt%  $\text{ZrO}_2$  (+  $\text{HfO}_2$ ) and 5.4 wt%  $\text{Y}_2\text{O}_3$ ; obtained under the trade designation "HSY 3.0" from Zirconia Sales, Inc. of Marietta, GA), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 136.5 grams of distilled water, and (b) the powders were present in amounts to provide 54.8 mole %  $\text{Al}_2\text{O}_3$  and 45.2 mole %  $\text{ZrO}_2$ . The fused material was white in color.

FIG. 10 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Example 1) of fused Comparative Example E material. The photomicrograph shows a eutectic derived microstructure comprising a plurality of colonies. The colonies were about 5-40 micrometers in size. Based on powder x-ray diffraction of a portion of Comparative Example E material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline  $\text{ZrO}_2$ , and the dark portions  $\alpha\text{-Al}_2\text{O}_3$ . The widths of these phases observed in the polished section were up to about 0.5 micrometer.

The average microhardness of Comparative Example E was determined, as described above in Example 1, to be 15.3 GPa.

Several Comparative Example E particles were heated placed in a platinum crucible and heated to 1000°C at 50°C/hour, held at 1000°C for 4 hours (in air), and then cooled to room temperature at about 100°C/hour. The color of the abrasive particles after heating was white. The average microhardness of the abrasive particles after heating was 15.0 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. An SEM photomicrograph Comparative Example E material before heating is shown in FIG. 15. The microstructure observed after heating was substantially the same as the microstructure observed before heating.

Further powder x-ray diffraction, as described above for Comparative Example B, was used to qualitatively measure the phases present in Comparative

Example E material before and after the above described heat-treatment by comparing the peak intensities of 111 of cubic and/or tetragonal reflection at about  $2\theta=30$  degrees,

to that of  $11\bar{1}$  of monoclinic reflection at about  $2\theta=28$  degrees. The unheat-treated

Comparative Example E material contained predominantly cubic and/or tetragonal zirconia before and after the heat-treatment (i.e., there was no significant difference noted in the x-ray diffraction results).

Several Comparative Example E particles were also heated placed in a platinum crucible and heated to 1000°C at 50°C/hour, held at 1000°C for 8 hours (in air), and then cooled to room temperature at about 100°C/hour. The color of the abrasive particles after heating was white. The average microhardness of the abrasive particles after heating was 15.0 GPa. The polished cross-sections prepared for the microhardness measurements were examined using the SEM in the secondary electron mode. The microstructure observed after heating was only slightly different than that observed before heating. An SEM photomicrograph Comparative Example E after heating is shown in FIG. 16. There was some cracks observed in the heat-treated material, generally near primary crystals of  $ZrO_2$ .

#### Differential Thermal Analysis (DTA) And Thermogravimetric Analysis (TGA) of Example 1 and Comparative Example B and E Abrasive Particles/Materials

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were conducted for each of Example 1 and Comparative Example B and E abrasive particles/materials. Each material was crushed with a mortar and pestle and screened to retain particles that were in the 400-500 micrometer size range.

DTA/TGA runs were made (using an instrument obtained from Netzsch Instruments, Selb, Germany under the trade designation "NETZSCH STA 409 DTA/TGA") for each of the screened samples. The amount of each screened sample placed in the 100 microliter  $Al_2O_3$  sample holder was 129.5 micrograms (Example 1), 125.8 micrograms (Comparative Example E), 127.3 micrograms (Comparative Example B), respectively. Each sample was heated in static air at a rate of 10°C/minute from room temperature (about 25°C) to 1300°C.

Referring to FIG. 5, line 157 is the plotted DTA data for the Example 1 material; line 159, the plotted TGA data. Referring to FIG. 6, line 177 is the plotted DTA data for the Comparative Example E material; line 179, the plotted TGA data. Referring to FIG. 7, line 187 is the plotted DTA data for the Comparative Example B material; line 189, the plotted TGA data. The change in weight of the sample through the TGA run was, for Example 1, 0.22%; for Comparative Example E, 0.73%; and, for Comparative Example B, 1.16%.

#### Example 2

Example 2 fused material, abrasive particles, and coated abrasive discs, were prepared as described in Example 1, except the polyethylene bottle was charged with 171.6 grams of alumina powder ("APA-0.5"), 83.4 grams of yttrium oxide powder (obtained from H.C. Starck, Newton, MA), 45 grams of zirconium oxide powder (with a nominal composition of 100 wt%  $\text{ZrO}_2$  (+  $\text{HfO}_2$ ); obtained under the trade designation "DK-2" from Zirconia Sales, Inc. of Marietta, GA), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 100 grams of distilled water. The fused material was white-red in color.

FIGS. 17 and 18 are scanning electron microscope (SEM) photomicrographs of a polished section (prepared as described in Example 1) of fused Example 2 material. Referring to FIGS. 17 and 18, the photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 5-30 micrometers in size. Based on powder x-ray diffraction of a portion of Example 2 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline cubic  $\text{ZrO}_2$ , the gray portions crystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and the dark portions  $\alpha$ - $\text{Al}_2\text{O}_3$ . The widths of these phases observed in the polished section were up to about 3 micrometers. Eutectic phases making up the colonies were in a lamellar arrangement. The alumina phases were seen as crystals exhibiting a trigonal shape. The orientation of at least a portion of the lamellar (i.e. orientation of eutectic crystallization) was observed to follow the orientation of the alumina in trigonal outline which was evident by an approximately 120 degree angle at which adjacent lamellar run into each other. While not wishing to be bounded by theory, it is believed that during crystallization of

the melt of a composition at or near ternary eutectic, primary alumina crystallized first as a seed in a trigonal shape. The consequent coupled growth of eutectic in the form of lamellar followed, at least initially, the orientation of the seed. A eutectic colony then included alumina seeds of the same orientation (or a single seed) together with the eutectic lamellar growth. Further, it was observed that the colony boundaries did not exhibit phase coarsening as was observed in the binary eutectic (manifested by the significant coarsening of crystals of eutectic phases in an immediate vicinity of colony boundary) of Example 1.

The average microhardness of Example 2 was determined, as described above in Example 1, to be 16.5 GPa.

Several Example 2 particles were heated placed in a platinum crucible and heated to 1000°C at 50°C/hour, held at 1000°C for 8 hours (in air), and then cooled to room temperature at about 100°C/hour. The color of the abrasive particles after heating was white. The average microhardness of the Example 2 particles after heating was 16.7 GPa.

#### Grinding Performance of Example 2 and Comparative Examples A-C

The grinding performance of Example 2 and Comparative Examples A-C coated abrasive discs were evaluated as described above for Example 1 and Comparative Examples A-C. The results are reported in Table 2, below.

Table 2		
Example	Total cut, g	Final cut, g
Comp. A	424	24
Comp. B	614	45
Comp. C	940	79
2	711	58

#### Example 3

Example 3 fused material was prepared as described in Example 1, except the polyethylene bottle was charged with 181.7 grams of alumina powder ("APA-0.5"), 88.3 grams of yttrium oxide powder (obtained from H.C. Starck, Newton, MA), 30 grams of zirconium oxide powder ("DK-2"), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 100 grams of distilled water.

FIG. 19 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Example 1) of fused Example 3 material. Referring to FIG. 19, the photomicrograph shows a ternary eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 10-40 micrometers in size. Based on powder x-ray diffraction of a portion of Example 3 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline cubic  $\text{ZrO}_2$ , the gray portions crystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and the dark portions  $\alpha\text{-Al}_2\text{O}_3$ . The widths of these phases observed in the polished section were up to about 5 micrometer. Further, large primary crystals (believed to be  $\text{Al}_2\text{O}_3$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), present in the form of dendrites, were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition.

#### Example 4

Example 4 fused material was prepared as described in Example 1, except the polyethylene bottle was charged with 141.3 grams of alumina powder ("APA-0.5"), 68.7 grams of yttrium oxide powder (obtained from H.C. Starck, Newton, MA), 90 grams of zirconium oxide powder ("DK-2"), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 100 grams of distilled water.

FIG. 20 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Example 1) of fused Example 4 material. Referring to FIG. 20, the photomicrograph shows a ternary eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 10-40 micrometers in size. Based on powder x-ray diffraction of a portion of Example 4 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline cubic  $\text{ZrO}_2$ , the gray portions crystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and the dark portions  $\alpha\text{-Al}_2\text{O}_3$ . The widths of these phases observed in the polished section were up to about 5 micrometers. Further, large primary crystals (believed to be  $\text{ZrO}_2$ ), present in the form of dendrites, were observed in some areas of the polished cross-section, indicating possible deviation of the composition from an exact eutectic composition.



### Example 5

Example 5 fused material was prepared as described in Example 1, except the polyethylene bottle was charged with 191.8 grams of alumina powder ("APA-0.5"), 93.2 grams of yttrium oxide powder (obtained from H.C. Starck, Newton, MA), 15 grams of zirconium oxide powder ("DK-2"), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 100 grams of distilled water.

FIG. 21 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Example 1) of fused Example 5 material. Referring to FIG. 21, the photomicrograph shows a binary eutectic-derived microstructure. Based on powder x-ray diffraction of a portion of Example 5 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline cubic  $\text{ZrO}_2$ , the gray portions crystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and the dark portions  $\alpha\text{-Al}_2\text{O}_3$ . The widths of these phases observed in the polished section were up to about 10 micrometers. Further, large primary crystals (believed to be  $\text{ZrO}_2$ ) were observed between crystals of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , indicating that deviation of the composition from an exact eutectic composition is quite large.

### Example 6

Example 6 fused material was prepared as described in Example 1, except the polyethylene bottle was charged with 201.9 grams of alumina powder ("APA-0.5"), 88.3 grams of yttrium oxide powder (obtained from H.C. Starck, Newton, MA), 9.8 grams of neodymium oxide powder (obtained from Molycorp, Inc., Brea, CA), 0.6 gram of a dispersing agent ("DURAMAX D-30005"), and 100 grams of distilled water.

FIG. 22 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Example 1) of fused Example 6 material. Referring to FIG. 22, the photomicrograph shows a eutectic-derived microstructure. Based on powder x-ray diffraction of a portion of Example 6 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were Nd-rich phase, the gray portions crystalline

yttrium aluminum garnet with some yttrium substituted by neodymium, and the dark portions  $\alpha$ - $\text{Al}_2\text{O}_3$ . The widths of these phases observed in the polished section were up to about 10 micrometers.

## 5 Example 7

Example 7 fused material, abrasive particles, and coated abrasive discs were prepared as described in Example 1, except (a) the polyethylene bottle was charged with 201.9 grams of alumina powder ("APA-0.5") and 98.1 grams of yttrium oxide powder (obtained from H.C. Starck, Newton, MA), and (b) the powders were  
10 present in amounts to provide 82 mole %  $\text{Al}_2\text{O}_3$  and 18 mole %  $\text{Y}_2\text{O}_3$ .

FIG. 23 is a scanning electron microscope (SEM) photomicrograph of a polished section (prepared as described in Example 1) of fused Example 7 material. Referring again to FIG. 23, the photomicrograph shows a eutectic-derived microstructure comprising a plurality of colonies. The colonies were about 10-40  
15 micrometers in size. Based on powder x-ray diffraction of a portion of Example 7 material, and examination of the polished sample using SEM in the backscattered mode, it is believed that the white portions in the photomicrograph were crystalline  $\text{Y}_3\text{Al}_5\text{O}_{12}$ , and the dark portions  $\alpha$ - $\text{Al}_2\text{O}_3$ . The widths of these phases observed in the polished section were up to about 1 micrometer.

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## Grinding Performance of Example 7 and Comparative Examples A-C

The grinding performance of Example 7 and Comparative Examples A-C coated abrasive discs were evaluated as described above for Example 1 and Comparative Examples A-C. The results are reported in Table 3, below.

25

Table 3

Example	Total cut, g	Final cut, g
Comp. A	431	25
Comp. B	674	50
Comp. C	933	78
7	787	56

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

What is claimed is:

1. Fused, crystalline abrasive particle comprising at least 20 percent by volume, based on the total metal oxide volume of said particle, eutectic material,  
5 wherein said eutectic material comprises eutectic of at least two of (a) crystalline  $\text{Al}_2\text{O}_3$ , (b) crystalline  $\text{Y}_2\text{O}_3$ , (c) a first crystalline, complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , or (d) a second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ .
2. The fused, crystalline abrasive particle according to claim 1  
10 comprising at least 50 percent by volume, based on the total metal oxide volume of said particle, of said eutectic material.
3. The fused, crystalline abrasive particle according to claim 2  
15 comprising, on a theoretical oxide basis, at least 40 percent by weight  $\text{Al}_2\text{O}_3$ , based on the total metal oxide content said particle.
4. The fused, crystalline abrasive particle according to claim 3,  
wherein said eutectic is  $\text{Al}_2\text{O}_3\text{-Y}_3\text{Al}_5\text{O}_{12}$  eutectic.
- 20 5. The fused, crystalline abrasive particle according to claim 3,  
wherein said fused, crystalline abrasive particle further comprises primary crystals of  $\text{Al}_2\text{O}_3$ .
6. The fused, crystalline abrasive particle according to claim 3,  
wherein said fused, crystalline abrasive particle comprises colonies of said eutectic, and  
25 wherein said colonies have an average size of less than 100 micrometers.
7. The fused, crystalline abrasive particle according to claim 6,  
wherein said colonies have an average size of less than 50 micrometers.

8. The fused, crystalline abrasive particle according to claim 3, wherein said fused, crystalline abrasive particle comprises colonies of said eutectic, and wherein crystals making up said colonies are, on average, up to 10 micrometers in size.

5 9. The fused, crystalline abrasive particle according to claim 8, wherein said crystals are, on average, up to 1 micrometer in size.

10 10. The fused, crystalline abrasive particle according to claim 3, wherein said fused, crystalline abrasive particle further comprises at least one of crystalline rare earth oxide or crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{rare earth oxide}$ .

11. The fused, crystalline abrasive particle according to claim 3, wherein said fused, crystalline abrasive particle further comprises at least one of crystalline BaO, CaO,  $\text{Cr}_2\text{O}_3$ , CoO,  $\text{Fe}_2\text{O}_3$ ,  $\text{HfO}_2$ ,  $\text{Li}_2\text{O}$ , MgO, MnO, NiO,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  
15  $\text{Na}_2\text{O}$ , SrO,  $\text{Sc}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ , ZnO,  $\text{ZrO}_2$ , or complex  $\text{Al}_2\text{O}_3 \cdot \text{metal oxide thereof}$ .

12. The fused, crystalline abrasive particle according to claim 3, wherein said fused, crystalline abrasive particle has an average microhardness of at least 13 GPa.

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13. The fused, crystalline abrasive particle according to claim 3, wherein said complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  further comprises cations in addition to Al and Y cations.

25 14. The fused, crystalline abrasive particle according to claim 3, wherein a portion of said complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  Al cations are substituted with at least one cation of an element selected from the group consisting of: Cr, Ti, Sc, Fe, Mg, Ca, Si, Co, and combinations thereof.

30 15. The fused, crystalline abrasive particle according to claim 3, wherein a portion of said complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  Y cations are substituted with at least

one cation of an element selected from the group consisting of: Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Th, Tm, Yb, and combinations thereof.

16. The fused, crystalline abrasive particle according to claim 3,  
5 wherein a portion of said complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$  Y cations are substituted with at least one cation of an element selected from the group consisting of: Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Mg, Ca, Sr, and combinations thereof.

17. The fused, crystalline abrasive particle according to claim 2, said  
10 fused, crystalline abrasive particle further comprises primary crystals of  $\text{Y}_3\text{Al}_5\text{O}_{12}$ .

18. A plurality of particles having a particle size distribution ranging from fine to coarse, wherein at least a portion of said plurality of particles are fused, crystalline abrasive particles comprising at least 20 percent by volume, based on the  
15 total metal oxide volume of the respective particle, eutectic material, wherein said eutectic material comprises eutectic of at least two of (a) crystalline  $\text{Al}_2\text{O}_3$ , (b) crystalline  $\text{Y}_2\text{O}_3$ , (c) a first crystalline, complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , or (d) a second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ .

19. A plurality of abrasive particles having a specified nominal  
20 grade, said plurality of abrasive particle having a particle size distribution ranging from fine to coarse, wherein at least a portion of said abrasive particles is a plurality of fused, crystalline abrasive particles, said fused abrasive particles comprising at least 20 percent by volume, based on the total metal oxide volume of the respective particle,  
25 eutectic material, wherein said eutectic material comprises eutectic of at least two of (a) crystalline  $\text{Al}_2\text{O}_3$ , (b) crystalline  $\text{Y}_2\text{O}_3$ , (c) a first crystalline, complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , or (d) a second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ .

20. A method for making fused, crystalline abrasive particles  
30 comprising at least 20 percent by volume, based on the total volume of the respective particle, eutectic material, wherein said eutectic material comprises eutectic of at least

two of (a) crystalline  $\text{Al}_2\text{O}_3$ , (b) crystalline  $\text{Y}_2\text{O}_3$ , (c) a first crystalline, complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , or (d) a second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , said method comprising:

- 5       melting at least one  $\text{Al}_2\text{O}_3$  source and at least one  $\text{Y}_2\text{O}_3$  source to  
provide a melt; and  
converting the melt to said fused, crystalline abrasive particles.

- 10       21.     The method according to claim 20, wherein converting includes:  
cooling the melt to provide a solidified material; and  
crushing the solidified material to provide said fused,  
crystalline abrasive particles.

- 15       22.     The method according to claim 21, wherein cooling the melt  
includes cooling the melt with metallic plates.

23.     The method according to claim 21, wherein cooling the melt  
includes cooling the melt with metallic balls.

- 20       24.     An abrasive article comprising a binder and a plurality of  
abrasive particles, wherein at least a portion of said abrasive particles are fused,  
crystalline abrasive particles comprising at least 20 percent by volume, based on the  
total volume of the respective particle, eutectic material, wherein said eutectic material  
comprises eutectic of at least two of (a) crystalline  $\text{Al}_2\text{O}_3$ , (b) crystalline  $\text{Y}_2\text{O}_3$ , (c) a  
first crystalline, complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , or (d) a second, different, crystalline complex  
25      $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ .

25.     The abrasive article according to claim 24, wherein said article is  
a coated abrasive article, and further comprises a backing.

- 30       26.     The abrasive article according to claim 24, wherein said article is  
a bonded abrasive article.

27. The abrasive article according to claim 24, wherein said article is a nonwoven abrasive article, and further comprises a nonwoven web.

5 28. A vitrified bonded abrasive article comprising a plurality of abrasive particles bonded together via vitrified bonding material, wherein at least a portion of said plurality of abrasive particles are fused, crystalline abrasive particles comprising at least 20 percent by volume, based on the total volume of the respective particle, eutectic material, wherein said eutectic material comprises eutectic of at least  
10 two of (a) crystalline  $\text{Al}_2\text{O}_3$ , (b) crystalline  $\text{Y}_2\text{O}_3$ , (c) a first crystalline, complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , or (d) a second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ .

29. The vitrified bonded abrasive article according to claim 28, wherein said vitrified bonding material comprises silica, alumina, and boria.

15 30. The vitrified bonded abrasive article according to claim 29, wherein said vitrified bonding material comprises at least 10 percent by weight of said alumina.

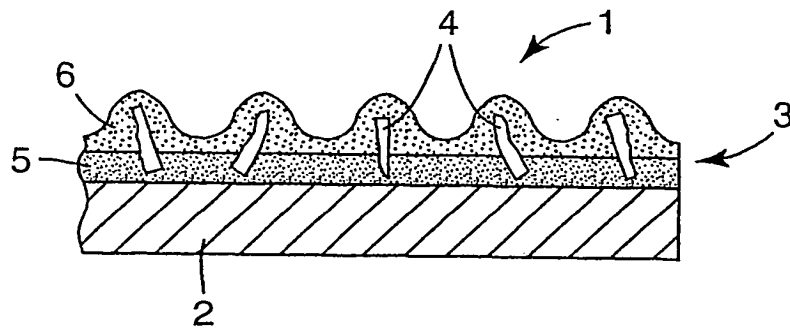
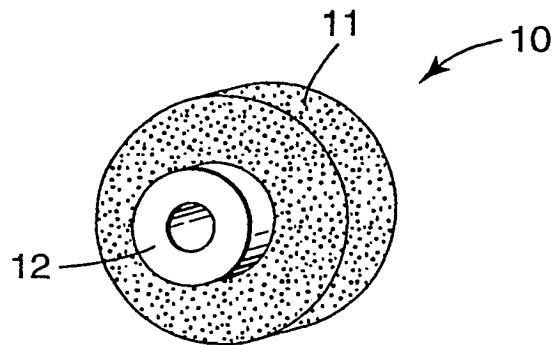
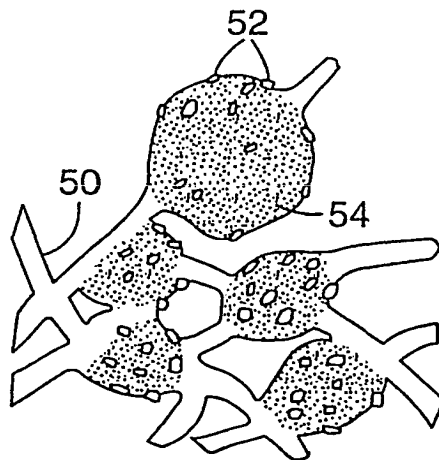
20 31. The vitrified bonded abrasive article according to claim 30, wherein said vitrified bonding material comprises at least 10 percent by weight of said boria.

25 32. A method of abrading a surface, said method comprising:  
contacting at least one fused, crystalline abrasive particle comprising at least 20 percent by volume, based on the total volume of the respective particle, eutectic material, wherein said eutectic material comprises eutectic of at least two of (a) crystalline  $\text{Al}_2\text{O}_3$ , (b) crystalline  $\text{Y}_2\text{O}_3$ , (c) a first crystalline, complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , or (d) a second, different, crystalline complex  $\text{Al}_2\text{O}_3 \cdot \text{Y}_2\text{O}_3$ , with a  
30 surface of a workpiece; and moving at least of one said fused abrasive particle or said

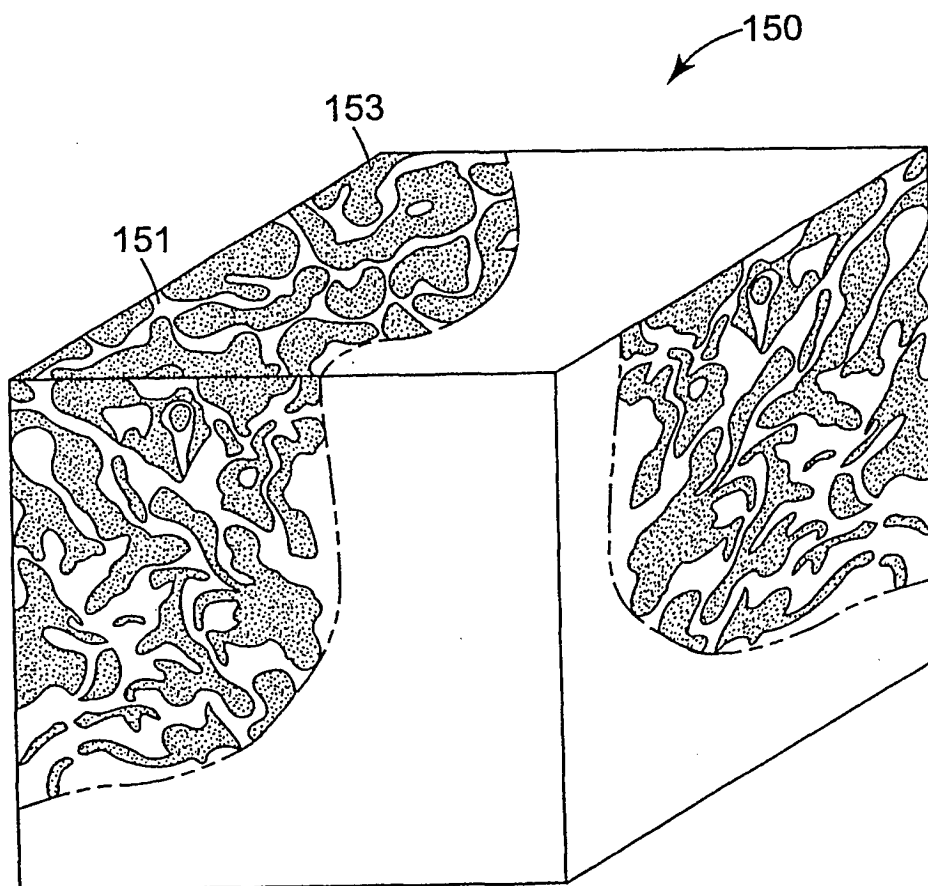


surface relative to the other to abrade at least a portion of said surface with said fused abrasive particle.

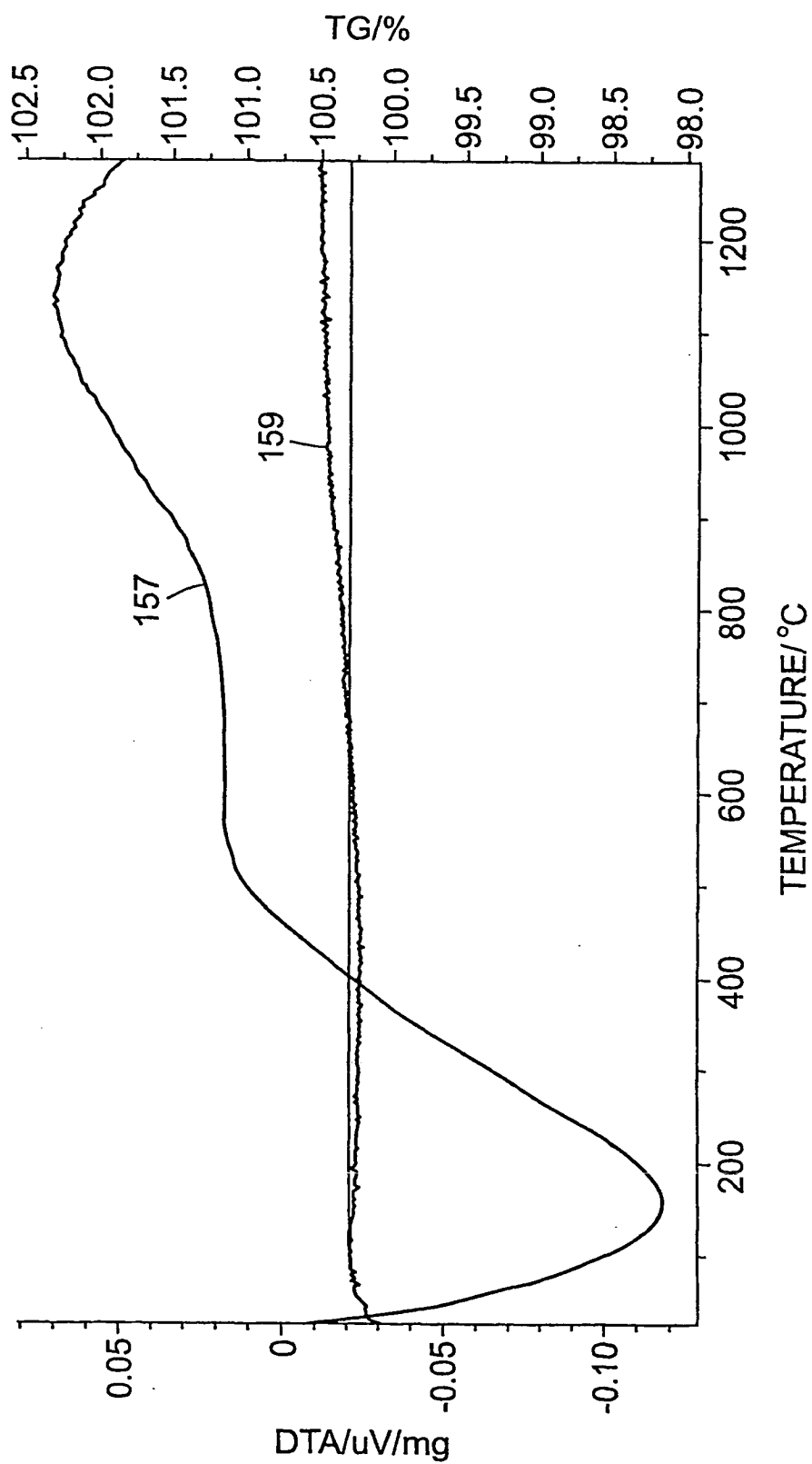
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*Fig. 1**Fig. 2**Fig. 3*

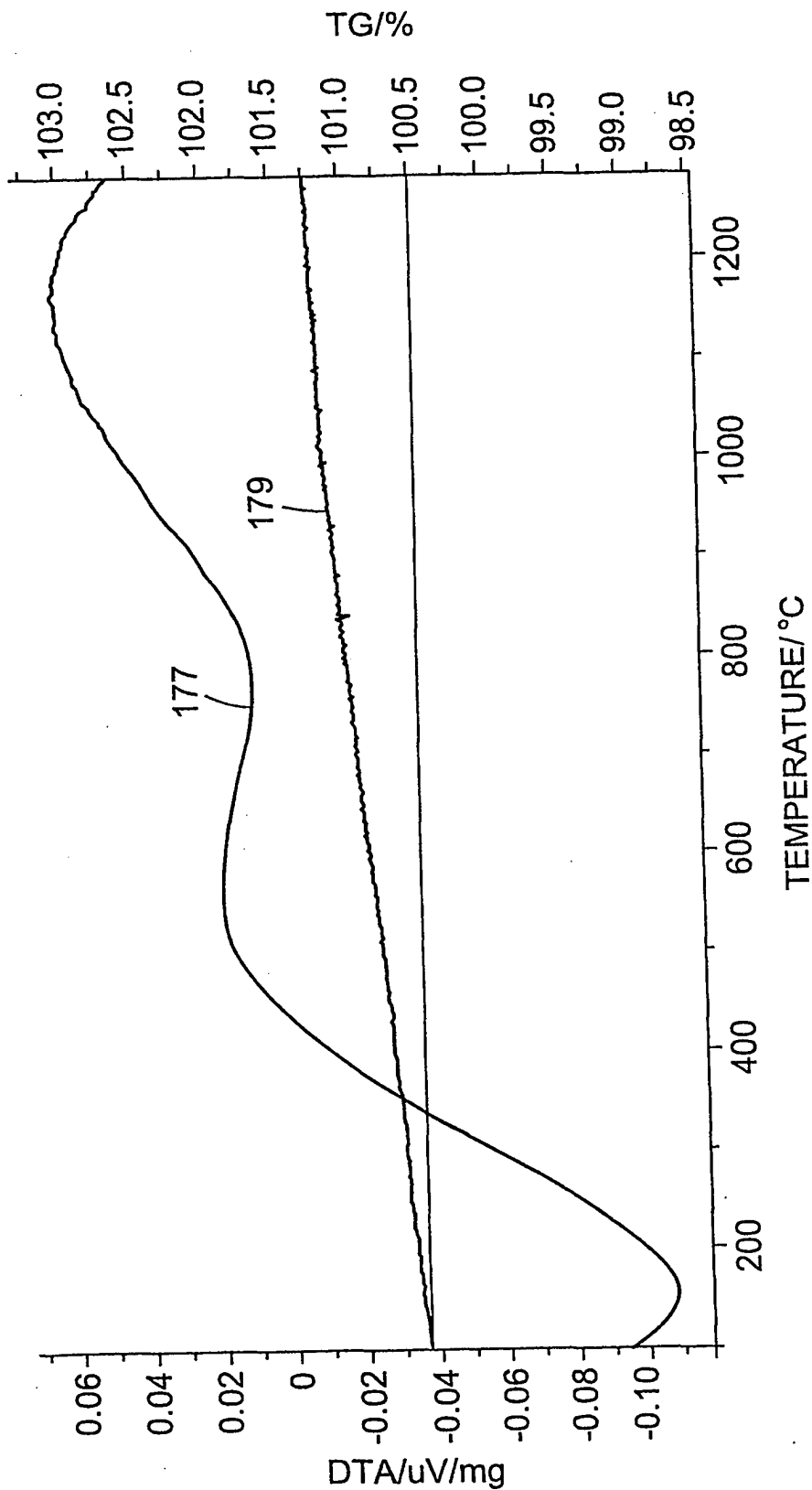
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**Fig. 4**

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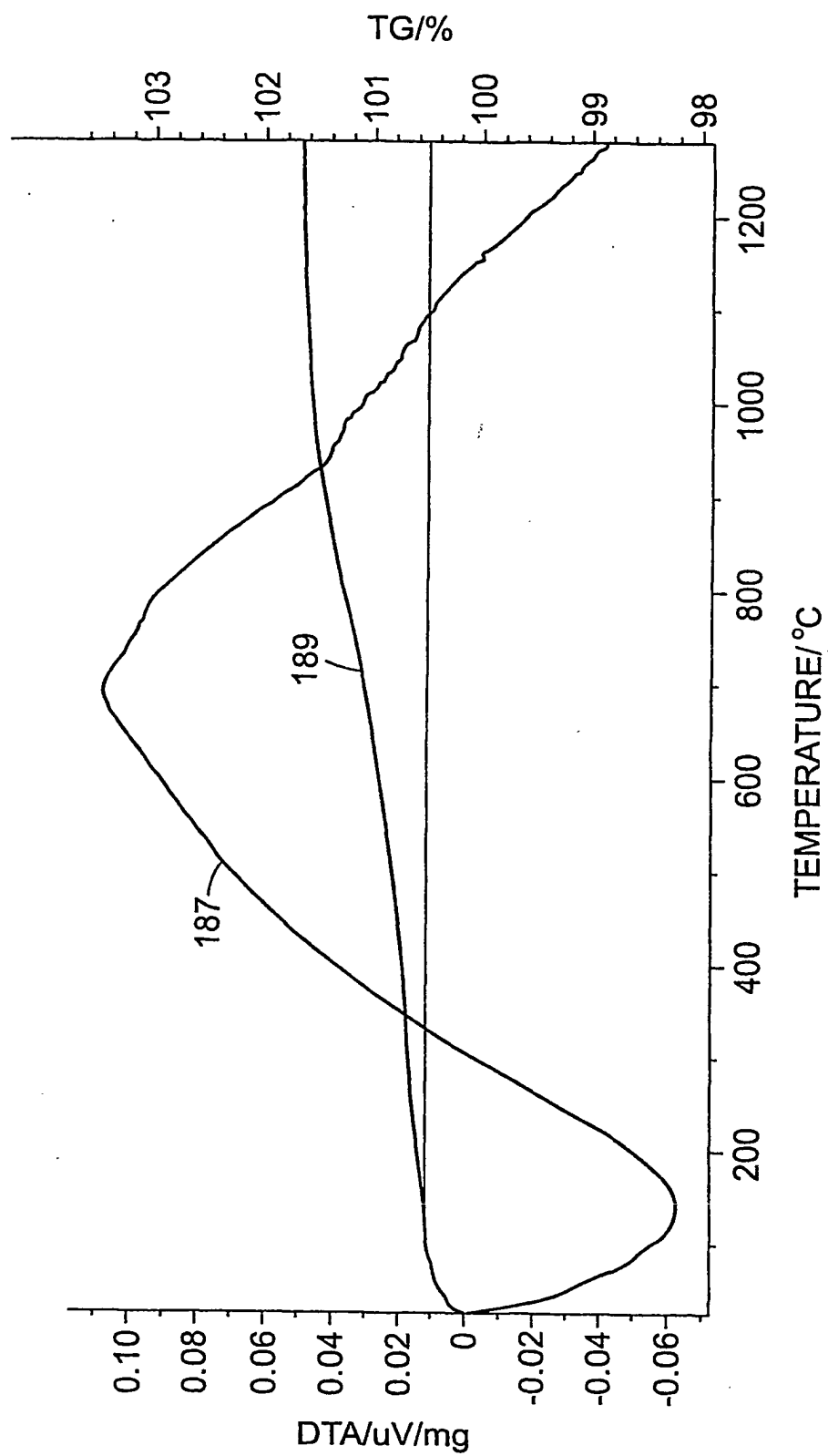
*Fig. 5*

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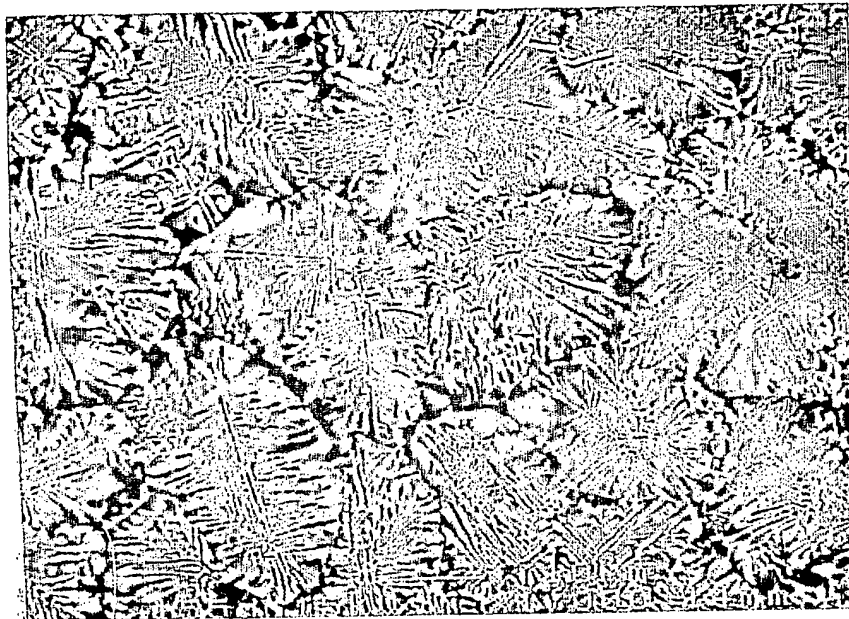


**Fig. 6**

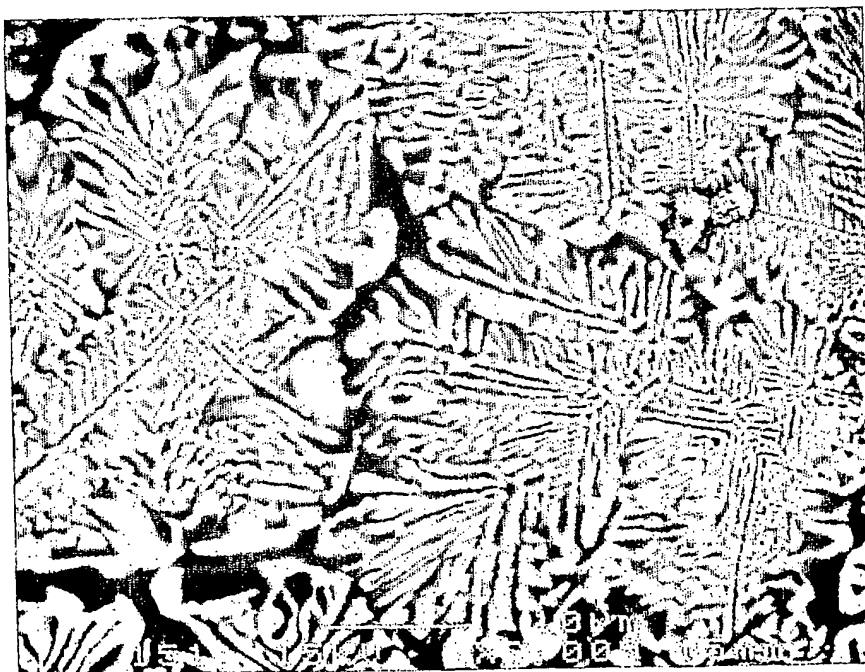
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*Fig. 7*

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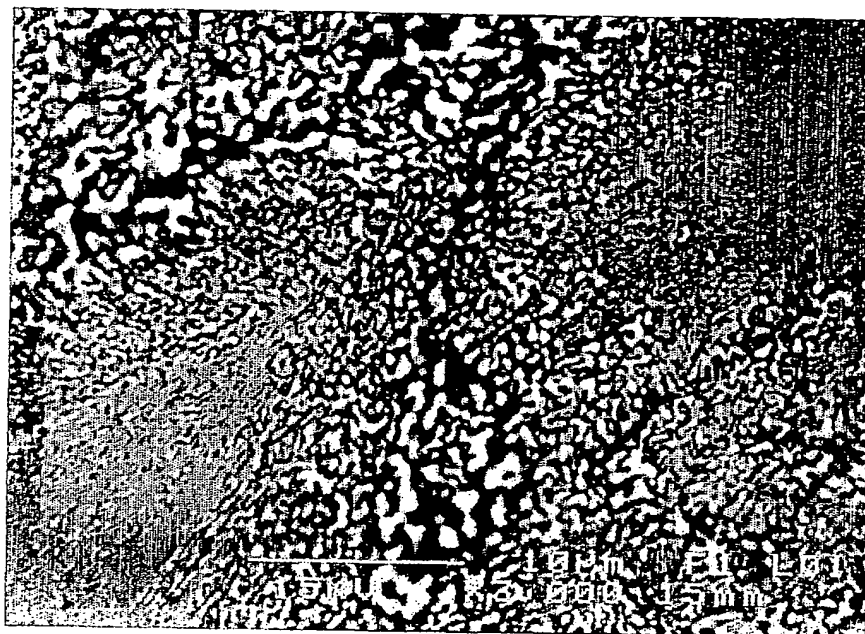


*Fig. 8*

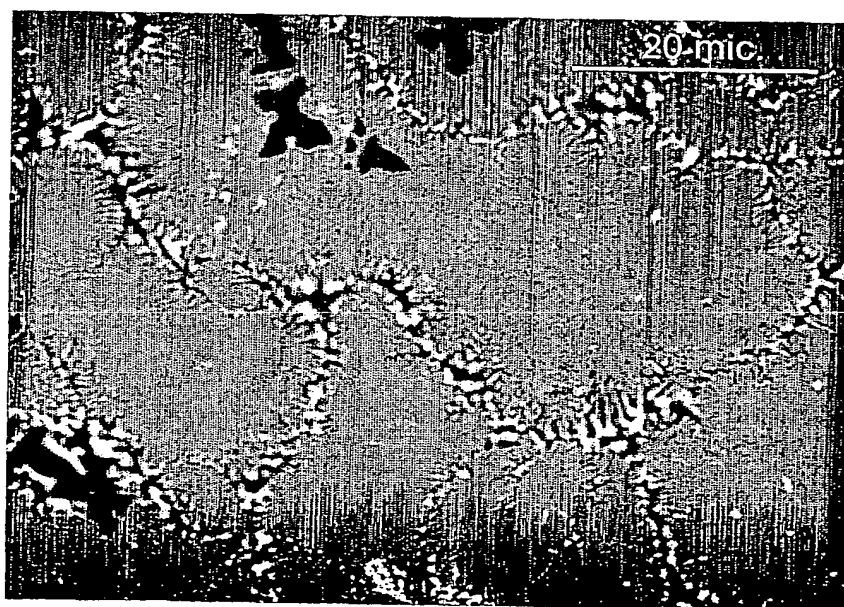


*Fig. 9*

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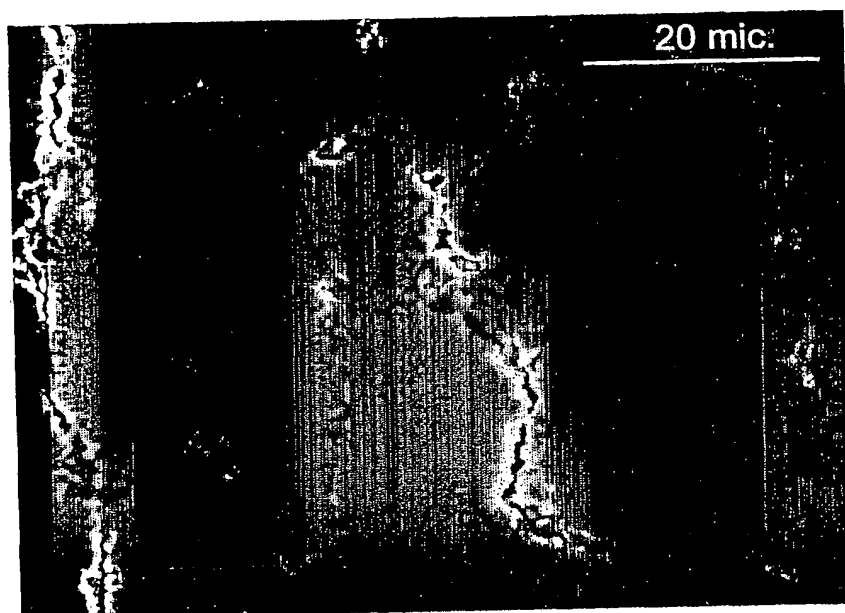
*Fig. 10*



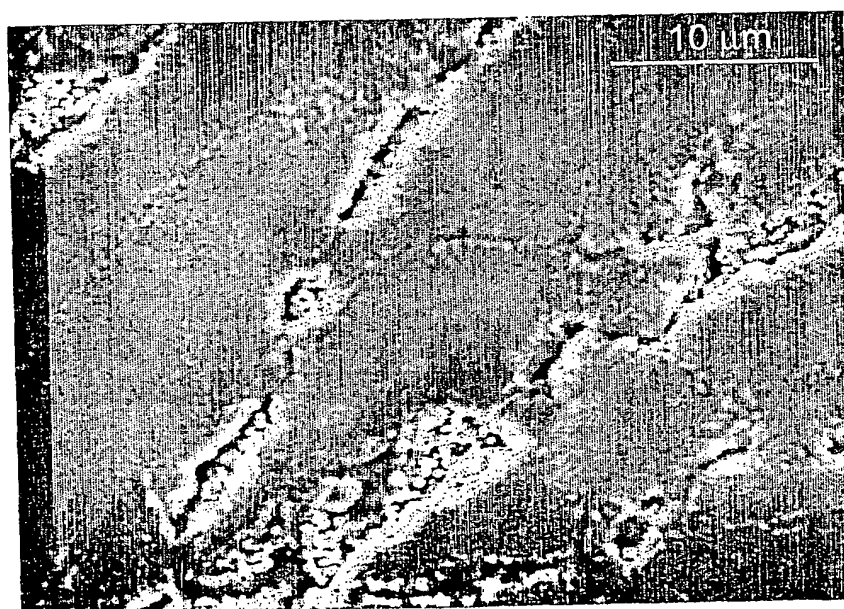
*Fig. 11*



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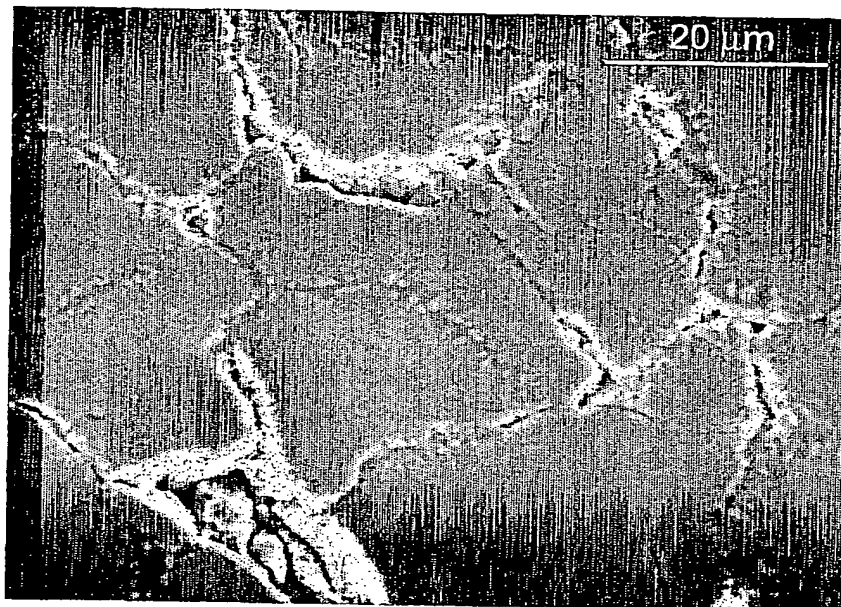


*Fig. 12*

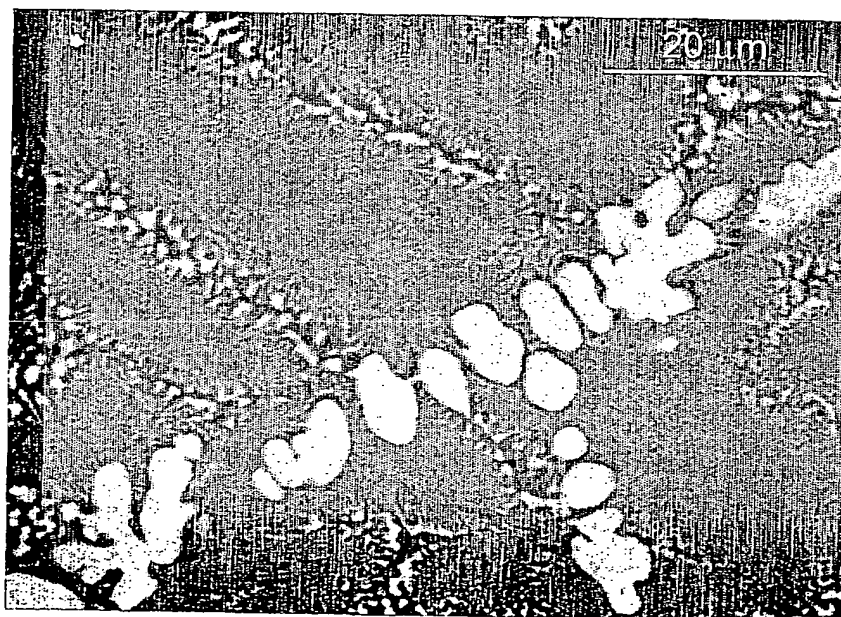


*Fig. 13*

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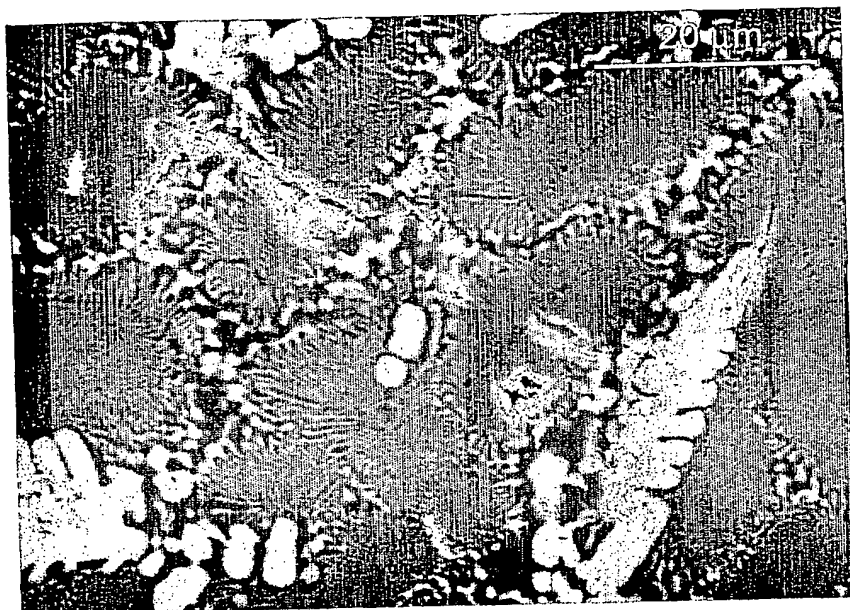


*Fig. 14*

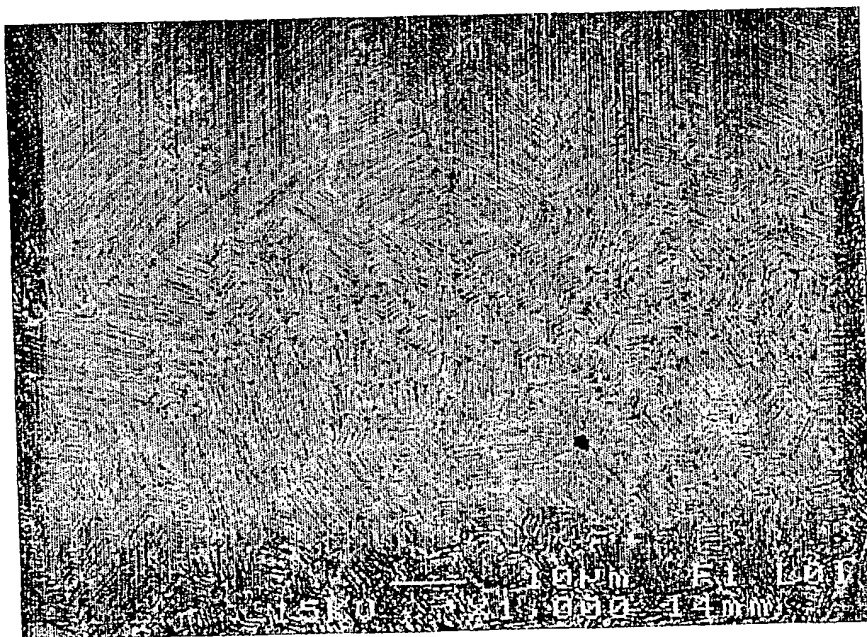


*Fig. 15*

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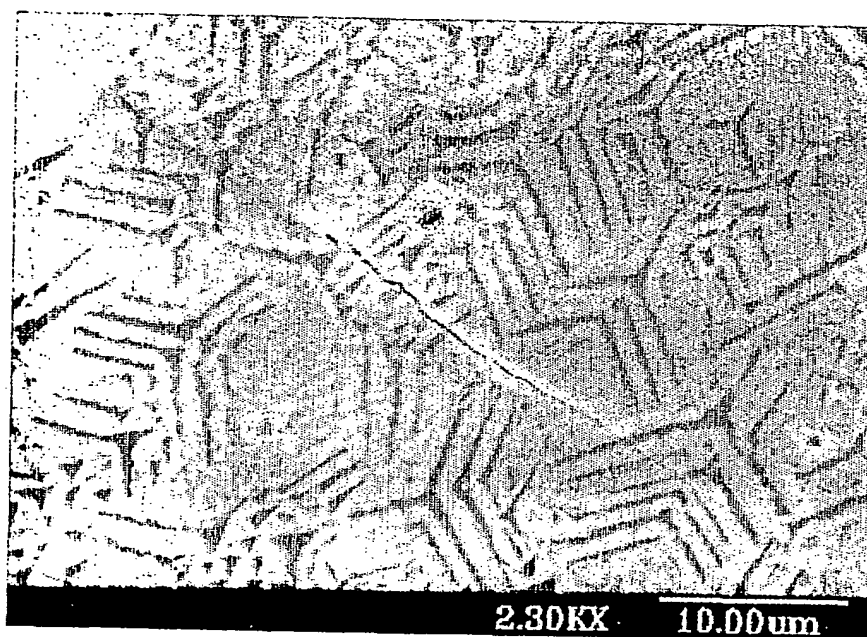


*Fig. 16*

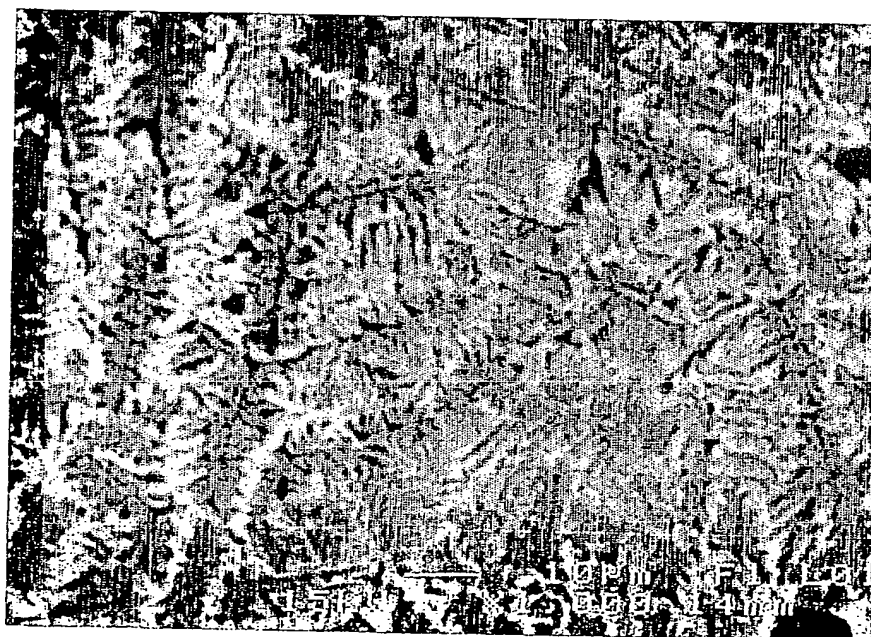


*Fig. 17*

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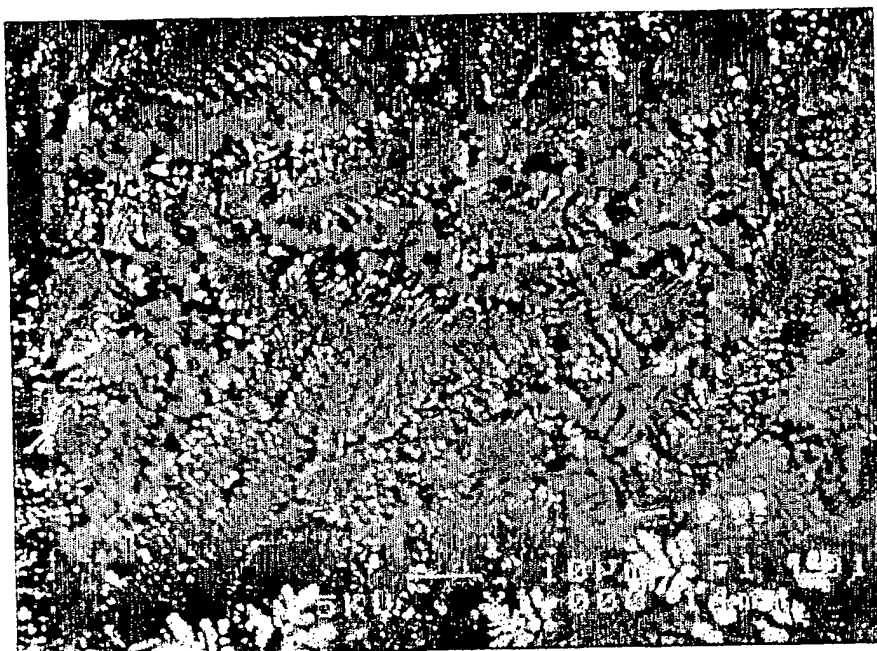


*Fig. 18*

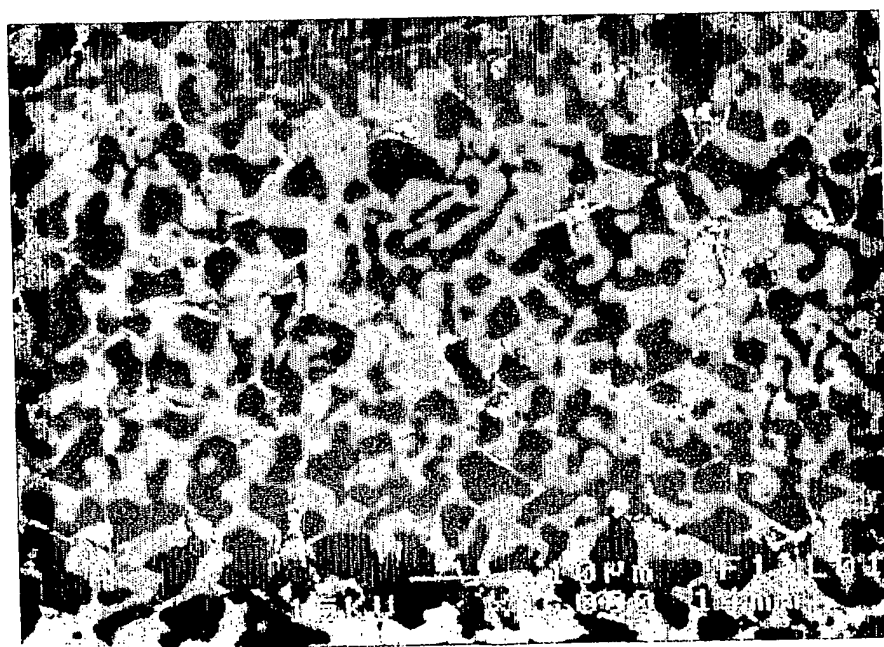


*Fig. 19*

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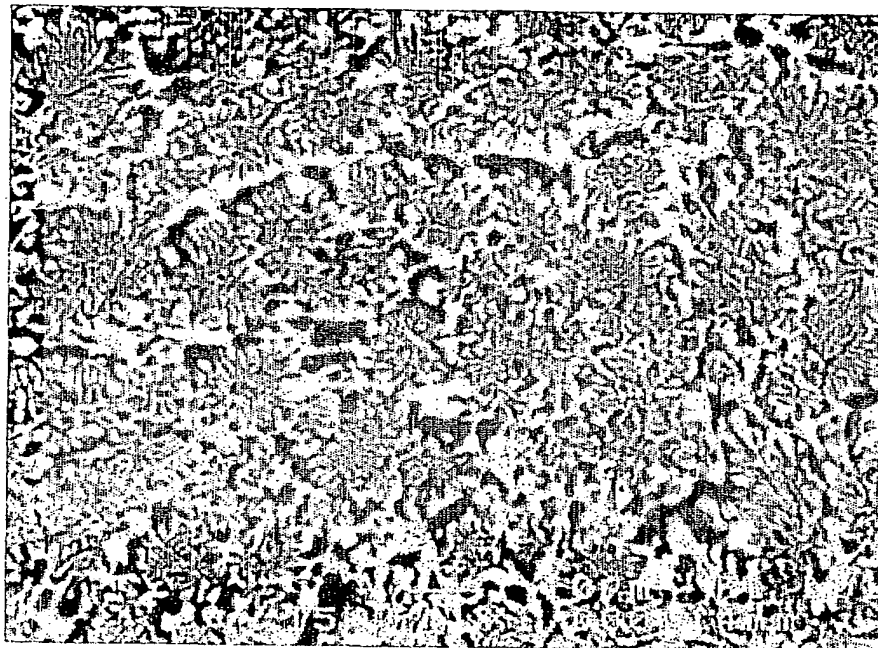
*Fig. 20*



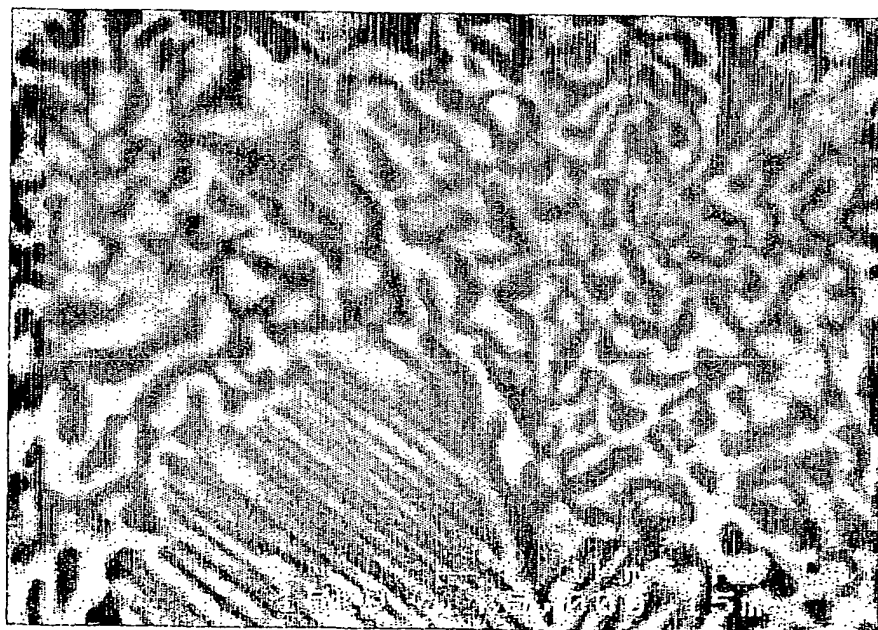
*Fig. 21*



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*Fig. 22*



*Fig. 23*

## INTERNATIONAL SEARCH REPORT

Int lonal Application No

PCT/US 01/03179

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C04B35/107 C04B35/117 C09K3/14 C04B35/111 C04B35/109  
B24D3/14 C03C14/00 C01F7/00 C01F11/18 C01G25/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C04B C09K B24D C03C C01F C01G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data, INSPEC, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BREWER L N ET AL: "Interface modification for increased fracture toughness in reaction-formed yttrium aluminum garnet/alumina eutectic composites" JOURNAL OF MATERIALS RESEARCH, OCT. 1999, MATER. RES. SOC, USA, vol. 14, no. 10, pages 3907-3912, XP001001121 ISSN: 0884-2914 the whole document --- -/--	1-21

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CHEMICAL ABSTRACTS 'Online!  CHEMICAL ABSTRACTS SERVICE, COLUMBUS,  OHIO, US;  VOLKOVA ET AL.: "Kinetics of nonisothermal  sintering of some eutectic oxide  compositions"  retrieved from STN  Database accession no. 105:10633 CA  XP002166786  abstract  &amp; IZV. VYSSH. UCHEBN. ZAVED., KHIM. KHIM.  TEKHNOL.,  vol. 29, no. 3, - 1986 pages 76-79,</p>	1-21
X	<p>EP 0 647 601 A (UBE INDUSTRIES)  12 April 1995 (1995-04-12)  page 3, line 26 -page 4, line 24; figure 3</p>	1-21
A	<p>US 4 770 671 A (MONROE LARRY D ET AL)  13 September 1988 (1988-09-13)  cited in the application  column 5, line 50 -column 6, line 19  column 7, line 56 -column 8, line 19;  tables 2,3</p>	1-32
A	<p>US 4 457 767 A (POON SIMON ET AL)  3 July 1984 (1984-07-03)  the whole document</p>	1-32



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/03179

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0647601 A	12-04-1995	JP 7149597 A	13-06-1995
		DE 69401416 D	20-02-1997
		DE 69401416 T	10-07-1997
		US 5569547 A	29-10-1996
US 4770671 A	13-09-1988	AT 72576 T	15-02-1992
		AU 590366 B	02-11-1989
		AU 6614586 A	02-07-1987
		BR 8606524 A	20-10-1987
		CA 1254392 A	23-05-1989
		DE 3683901 A	26-03-1992
		EP 0228856 A	15-07-1987
		ES 2027965 T	01-07-1992
		JP 1627762 C	28-11-1991
		JP 2053475 B	16-11-1990
		JP 62190279 A	20-08-1987
		KR 9401527 B	23-02-1994
		MX 166443 B	11-01-1993
		NO 174513 B	07-02-1994
		ZA 8609150 A	27-07-1988
US 4457767 A	03-07-1984	AT 26855 T	15-05-1987
		AU 573625 B	16-06-1988
		AU 3353684 A	04-04-1985
		BR 8404844 A	13-08-1985
		CA 1207153 A	08-07-1986
		DE 3463393 D	04-06-1987
		EP 0140164 A	08-05-1985
		ES 536206 D	16-07-1985
		ES 8506782 A	16-11-1985
		IN 162220 A	16-04-1988
		JP 1765216 C	11-06-1993
		JP 3012597 B	20-02-1991
		JP 60099567 A	03-06-1985
		ZA 8407230 A	27-11-1985

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